Iron-Catalyzed C-F Bond Silylation and Borylation of Aryl Fluorides

List of Contents

General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) or 600MR DD2 (600 MHz) spectrometer at ambient temperature. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet. NMR yield was determined by ^{1}H NMR using mesitylene as an internal standard before working up the reaction.

Materials: All reagents that used were from commercial sources, unless otherwise specified. Fe(OAc)$_2$ (95%) was purchased from Sigma-Aldrich. t-BuONa (99%) was purchased from Adamas. Cyclohexane and DMF were distilled under reduced pressure from CaH$_2$. 1,4-dioxane, THF, MTBE, (i-Pr)$_2$O, Xylene and toluene were distilled from sodium and benzophenone immediately before used.

Optimization of Iron-Catalyzed Silylation of Aryl Fluorides (Table S1-S7):

Table S1. Screening of Solvents.[a]

Entry	Solvent	Yield[b]
1	1,4-dioxane	15%
2	THF	18%
3	**Cyclohexane**	**27%**
4	Toluene	0%
5	DMF	0%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (3.5 equiv), Fe(OAc)$_2$ (10 mol%), t-BuONa (2.5 equiv), Solvent (1.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.
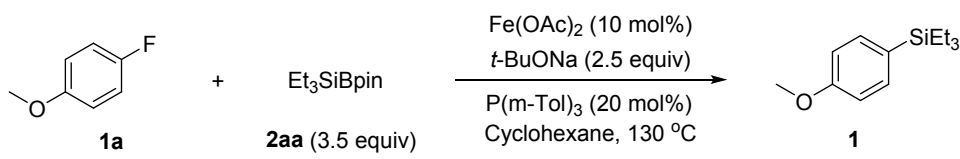
Table S2. Screening of Bases.[a]

Entry	Base	Yield[b]
1	K$_3$PO$_4$	0%
2	K$_2$CO$_3$	0%
3	Cs$_2$CO$_3$	0%
4	t-BuOK	Trace
5	**t-BuONa**	**27%**
6	none	0%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (3.5 equiv), Fe(OAc)$_2$ (10 mol%), Base (2.5 equiv), Cyclohexane (1.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.
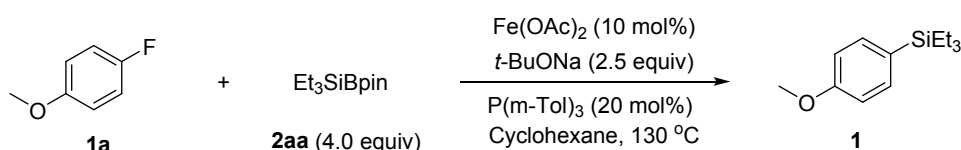
Table S3. Screening of Ligands.[a]

Entry	Ligand	Yield[b]

3

1	XantPhos	28%
2	PPh₃	34%
3	SPhos	31%
4	**P(m-tol)₃**	**54%**
5	X-Phos	27%
6	DPPE	43%
7	DPPH	36%
8	DPEPhos	34%
9	DPPF	42%
10	TMEDA	22%
11	Bathophenanth roline	12%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (3.5 equiv), Fe(OAc)₂ (10 mol%), t-BuONa (2.5 equiv), Cyclohexane (1.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ¹H NMR using trichloromethane as an internal standard.

Table S4. Screening of the loading of 2aa.[a]

Entry	Equiv	Yield[b]
1	2.5	27%
2	3.0	46%
3	3.5	54%
4	**4.0**	**64%**
5	4.5	60%
6	5.0	62%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (X equiv), Fe(OAc)₂ (10 mol%), t-BuONa (2.5 equiv), Cyclohexane (1.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ¹H NMR using trichloromethane as an internal standard.
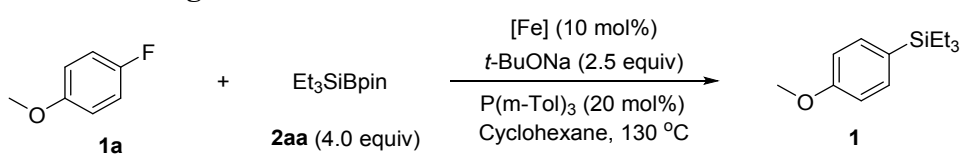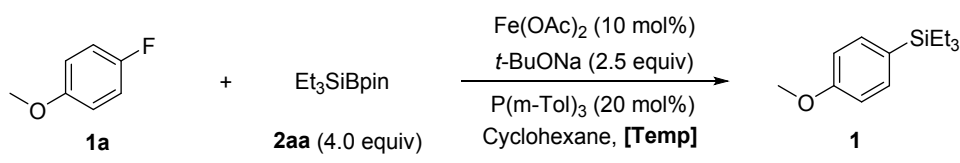
Table S5. Screening of the Concentration.[a]

Entry	Cyclohexane (X ml)	Yield[b]

1	0.5	51%
2	**0.8**	**72% (70%)**
3	1.0	64%
4	1.2	58%
5	1.5	42%
6	2.0	28%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (4.0 equiv), Fe(OAc)$_2$ (10 mol%), *t*-BuONa (2.5 equiv), Cyclohexane (X mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S6. Screening of Iron Sources.[a]

Entry	[Fe]	Yield[b]
1	Fe(acac)$_3$	62%
2	FeCl$_2$	0%
3	FeBr$_2$	Trace
4	Ferric Stearate	51%
5	Fe(acac)$_3$	45%
6	Fe(OTf)$_2$	58%
7	**Fe(OAc)$_2$**	**72% (70%)**

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (4.0 equiv), [Fe] (10 mol%), *t*-BuONa (2.5 equiv), Cyclohexane (0.8 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S7. Screening of temperature.[a]

Entry	[Temp]	Yield[b]
1	120 °C	63%
2	125 °C	65%
3	130 °C	72%
4	**135 °C**	**(75%)**

	5	140 °C	68%

Optimization of Iron-Catalyzed Borylation of Aryl Fluorides (Table S8-S13):

Table S8. Screening of Solvents.[a]
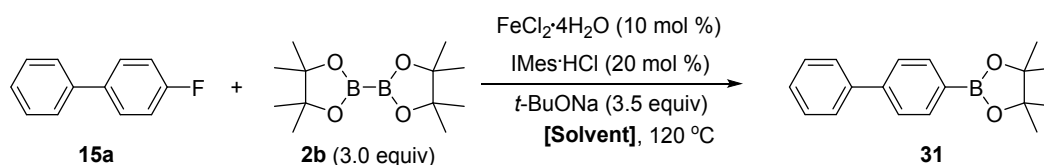
Entry	Solvent	Yield[b]
1	1,4-dioxane	**12%**
2	DME	6%
3	Cyclohexane	5%
4	Xylene	Trace
5	Isopropyl ether	Trace

Table S9. Screening of Bases.[a]
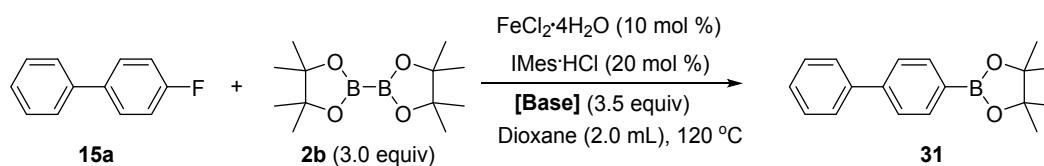
Entry	[Base]	Yield[b]
1	t-BuONa	**9%**
2	t-BuOMg	0%
3	KOMe	Trace
4	Li$_2$CO$_3$	0%
5	Na$_3$PO$_4$	0%
6	CsOAc	0%
7	KOAc	0%
8	Cs$_2$CO$_3$	0%
9	NaOAc	0%

10	CsF	0%
11	LiOAc	0%

[a]Reaction conditions (unless otherwise specified): **15a** (0.2 mmol, 1.0 equiv), **2b** (3.0 equiv), FeCl$_2$·4H$_2$O (10 mol%), Base (3.5 equiv), Dioxane (2.0 mL), 120 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S10. Screening of Ligands and temperature.[a]
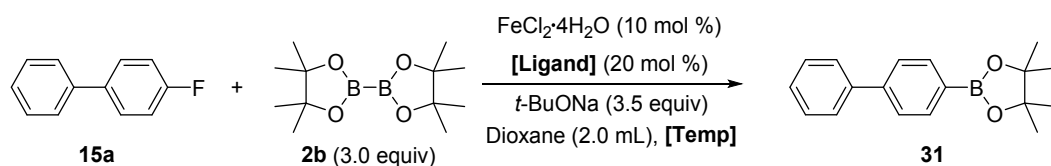
Entry	ligand	120 °C	130 °C	140 °C
1	TMEDA	12%	21%	9%
2	IMes·HCl	8%	11%	14%
3	SIMes·HCl	24%	37%	35%
4	IPr·HCl	9%	21%	24%

[a]Reaction conditions (unless otherwise specified): **15a** (0.2 mmol, 1.0 equiv), **2b** (3.0 equiv), FeCl$_2$·4H$_2$O (10 mol%), t-BuONa (3.5 equiv), Dioxane (2.0 mL), T °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S11. Screening of Iron Sources.[a]
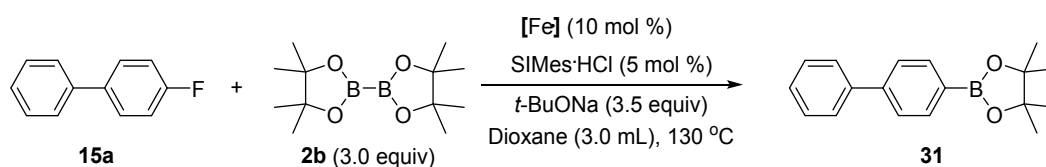
Entry	[Fe]	Yield[b]
1	FeI$_2$	11%
2	Fe(OTf)$_2$	6%
3	FeCl$_2$·4H$_2$O	30%
4	Fe(acac)$_3$	**46%**
5	Fe(OAc)$_2$	22%
6	FeBr$_2$	38%

[a]Reaction conditions (unless otherwise specified): **15a** (0.3 mmol, 1.0 equiv), **2b** (3.0 equiv), t-BuONa (3.5 equiv), Dioxane (3.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S12. Screening of the Concentration.[a]
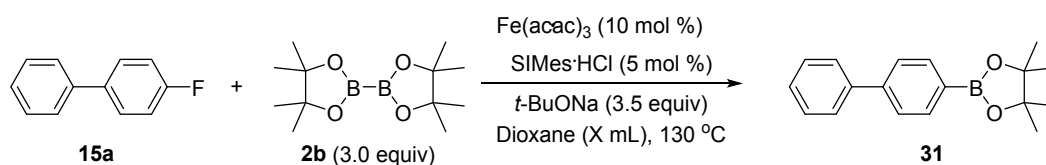
Entry	Dioxane (mL)	Yield[b]
1	1.5	48%
2	2.0	**58%**
3	2.5	41%
4	3.0	46%

[a]Reaction conditions (unless otherwise specified): **15a** (0.3 mmol, 1.0 equiv), **2b** (3.0 equiv), Fe(acac)$_3$ (10 mol %), t-BuONa (3.5 equiv), Dioxane (X mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S13. Screening of the Loading of Base.[a]
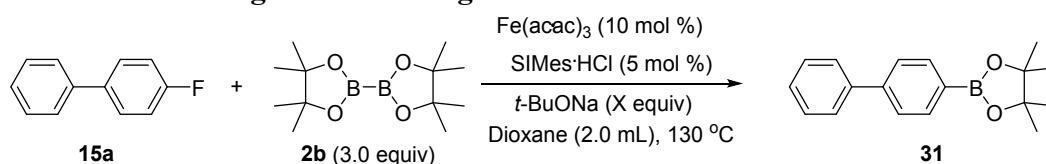
Entry	t-BuONa (equiv)	Yield[b]
1	3.5	56%
2	**4.0**	**(71%)**
3	4.5	49%
4	5.0	26%
5	5.5	Trace
6	6.0	Trace

[a]Reaction conditions (unless otherwise specified): **15a** (0.3 mmol, 1.0 equiv), **2b** (3.0 equiv), Fe(acac)$_3$ (10 mol %), t-BuONa (X equiv), Dioxane (2.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

## Table S14. Screening of Ligands Using 28a as the Substrate.[a]
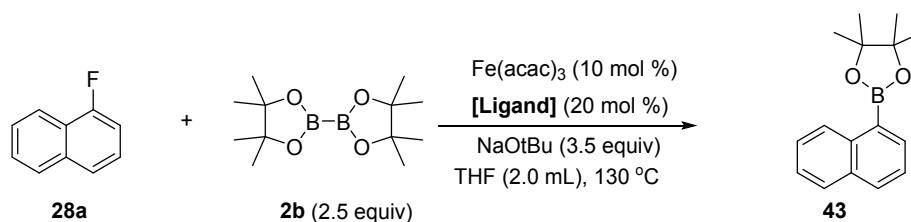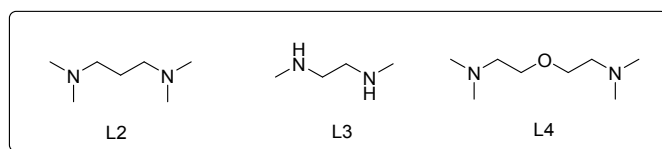
Entry	Ligand	Yield[b]
1	TMEDA	**75%**
2	TMMDA	70%
3	TEEDA	76%(71%)
4	L3	55%
5	L2	76%
6	L4	**79%(76%)**

[a]Reaction conditions (unless otherwise specified): **28a** (0.3 mmol, 1.0 equiv), **2b** (2.5 equiv), Fe(acac)$_3$ (10 mol %), t-BuONa (3.5 equiv), THF (2.0 mL), 130 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S15. Control Experiments.[a]
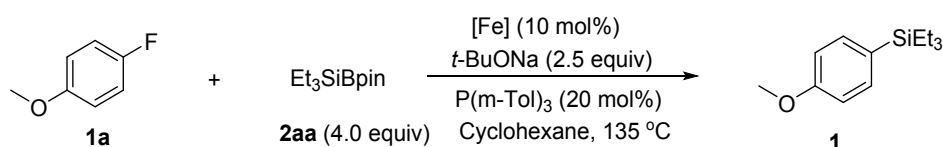
| Entry	[cat.]	Base	Ligand	Yield[b]
1	Fe(OAc)$_2$	t-BuONa	P(m-tol)$_3$	73%(75%)
2	Fe(OAc)$_2$ (99.99%)	t-BuONa	P(m-tol)$_3$	73%
3	Fe(OAc)$_2$	t-BuONa	-	24%
4	-	t-BuONa	P(m-tol)$_3$	3%
5	Fe(OAc)$_2$	-	P(m-tol)$_3$	-
6	Cu(OAc)$_2$ (5 mol%)	t-BuONa	P(m-tol)$_3$	8%
7	Cu(OAc)$_2$ (1 mol%)	t-BuONa	P(m-tol)$_3$	2%
8	Pd(OAc)$_2$ (5 mol%)	t-BuONa	P(m-tol)$_3$	45%
9	Ni(OAc)$_2$ (5 mol%)	t-BuONa	P(m-tol)$_3$	22%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (3.5 equiv), t-BuONa (2.5 equiv), Cyclohexane (0.8 mL), 135 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.
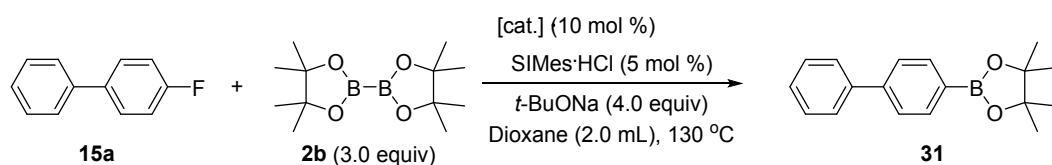
Entry	[cat.]	Base	Ligand	Yield[b]
1	Fe(acac)$_3$	t-BuONa	SIMes·HCl	(71%)
2	Fe(acac)$_3$ (99.99%)	t-BuONa	SIMes·HCl	70%
3	Fe(acac)$_3$	t-BuONa	-	20%
4	-	t-BuONa	SIMes·HCl	-
5	Fe(acac)$_3$	-	SIMes·HCl	-
6	Cu(OAc)$_2$	t-BuONa	SIMes·HCl	20%
7	Cu(OTf)$_2$	t-BuONa	SIMes·HCl	-
8	Pd(OAc)$_2$	t-BuONa	SIMes·HCl	45%
9	Ni(OAc)$_2$	t-BuONa	SIMes·HCl	10%
10	CuBr$_2$	t-BuONa	SIMes.HCl	-

[a]Reaction conditions (unless otherwise specified): **15a** (0.3 mmol, 1.0 equiv), **2b** (3.0 equiv), t-BuONa (4.0 equiv), Dioxane (2.0 mL), 130 ºC, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Table S16. Evaluation of Trace Metals Present in Commercial Iron Sources.

Trace-metal analysis: Fe(OAc)$_2$ (99.99%), Alfa Aesar	
Element	Molar Concentration
Cu	<0.66 ppm
Pd	<0.16 ppm
Ni	<0.67 ppm

Mechanistic Studies

Table S17. Radical Inhibition Experiments of Iron-Catalyzed Silylation of 1a and Borylation of 15a.[a]
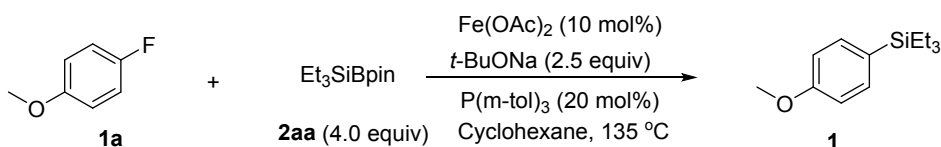
Entry	Additive (equiv)	Yield[b]
1	none	(75%)
2	TEMPO (1.0)	22%
3	BHT (1.0)	20%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (4.0 equiv), Fe(OAc)$_2$ (10 mol%), t-BuONa (2.5 equiv), Cyclohexane (0.8 mL), 135 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.
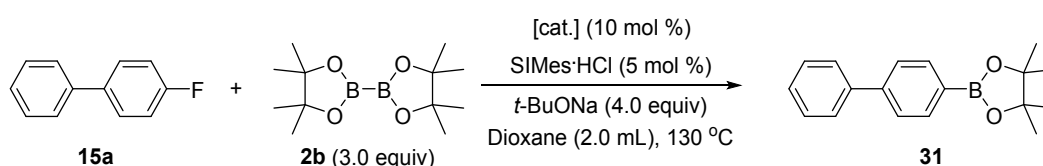
Entry	Additive (equiv)	Yield[b]
1	none	(71%)
2	TEMPO (1.0)	48%
3	BHT (1.0)	41%

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2aa** (4.0 equiv), Fe(OAc)$_2$ (10 mol%), t-BuONa (2.5 equiv), Cyclohexane (0.8 mL), 135 °C, 12 h, under an argon atmosphere. [b]Determined by ^{1}H NMR using trichloromethane as an internal standard.

Drastically diminished yields were observed when one equivalent of radical scavenger TEMPO, or radical inhibitor BHT was added under the standard silylation and borylation reaction conditions, indicating that a radical pathway might be involved.

Competitive experiment.[a]
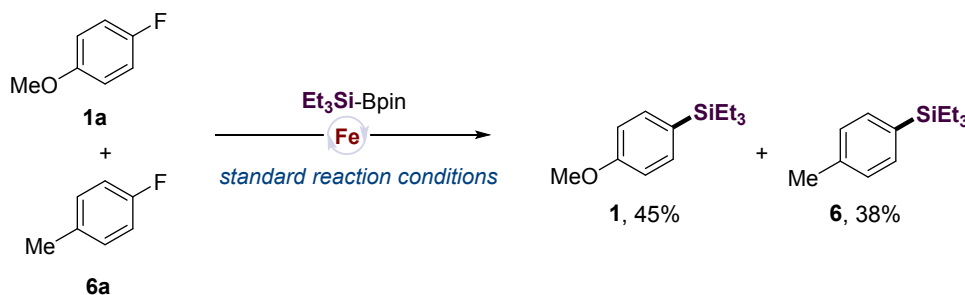
A better yield (45%) could be obtained using electron-rich **1a** as a substrate. Thus, these results indicate that this iron-catalyzed silylation is unlikely to occur through the $S_N Ar$ mechanism.

Control Experiments
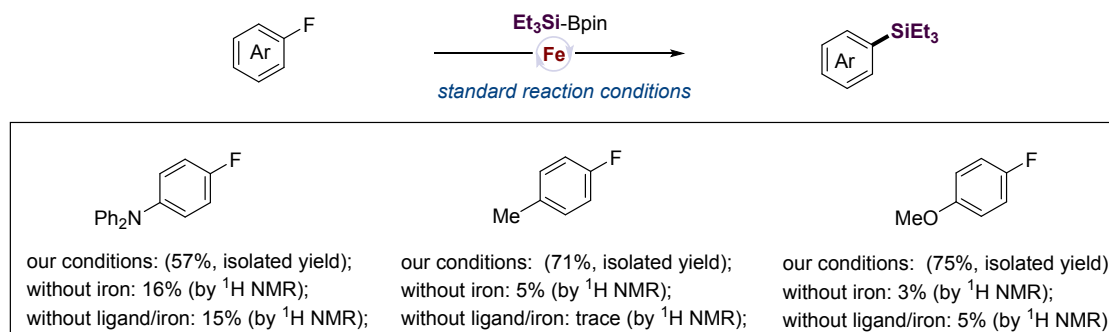
Some substrates with different electronic properties were chosen to conduct the control experiments. As shown, the desire product were only obtained in trace to 16% yield without iron. Therefore, these results suggest that this transformation is promoted by iron catalysis.

XPS Experiments

In order to gain further insight into the iron-catalyzed C-F bond activation reaction, the X-ray photoelectron spectroscopy (XPS) analysis was conducted bellow.

X-Ray Photoelectron Spectroscopy (XPS) Analysis of Aryl Fluoride

Procedure: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with Fe(OAc)$_2$ (3.5 mg, 0.02 mmol, 0.1 equiv), P(m-tol)$_3$ (12 mg, 0.04 mmol, 0.2 equiv), t-BuONa (48.1 mg, 0.5 mmol, 2.5 equiv) in glove box. Aryl Fluoride **1a** (0.2 mmol), fresh distilled silylborane **2aa** (4.0 equiv), fresh distilled cyclohexane (0.8 mL) were then added under nitrogen atmosphere. The reaction mixture was allowed to stir at 135 °C in oil bath for 1 h via heating mantle. Then, the reaction was cooled to

room temperature and concentrated under N_2. The resulting mixture was analyzed by X-ray photoelectron spectroscopy (XPS).
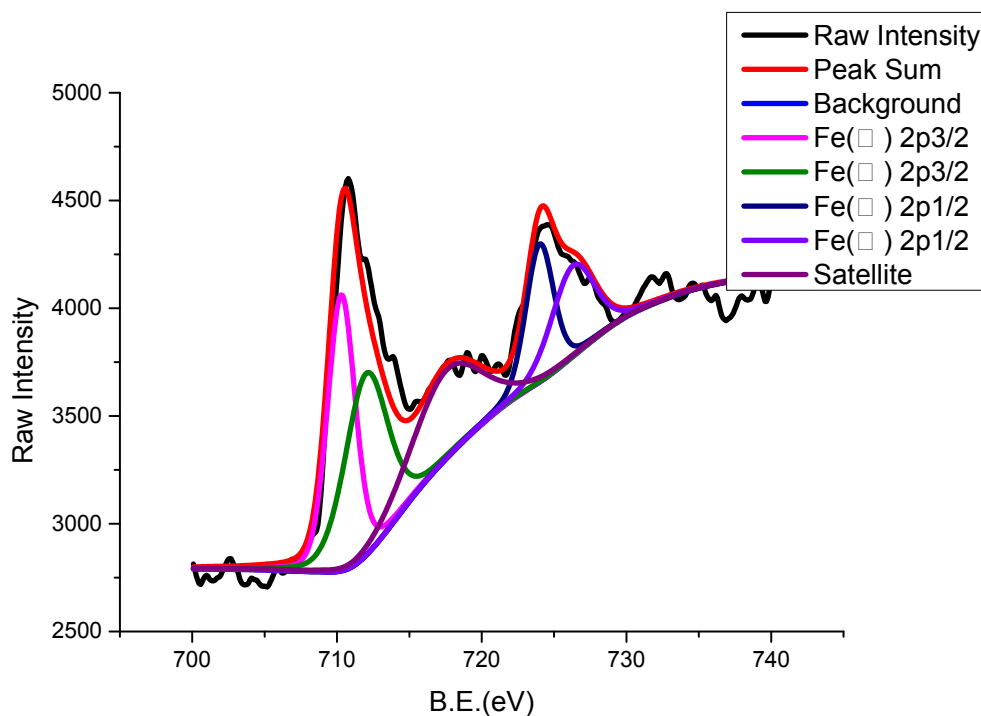
Peak	Position (eV)	Area	FWHM (eV)	%GL
0	710.300	3362.000	2.250	20
1	712.000	3434.000	3.490	20
2	724.000	1681.000	2.250	20
3	726.300	1717.000	3.490	20
4	717.565	2727.513	5.689	20

X-Ray Photoelectron spectroscopy (XPS) analysis of the reaction mixture of Fe(OAc)$_2$, t-BuONa, 1a and Et$_3$SiBpin.

Conclusion: When we studied the X-ray photoelectron spectroscopy (XPS) analysis of the reaction mixture of Fe(OAc)$_2$, t-BuONa and Et$_3$SiBpin. The experiments showed that peak corresponding to Fe^{II} 2p$_{3/2}$ was observed with the binding energy at 710.3 eV (compared with FeO).[15] What's more, when the reaction mixture under standard reaction condition was analyzed by XPS, both Fe^{II} 2p$_{3/2}$ and Fe^{III} 2p$_{3/2}$ were found with the binding energy at 710.3 eV (compared with FeO) and 712.0 eV (compared with

FePO$_4$).[16] Thus, these results demonstrated that Fe^{II} and Fe^{III} species might be involved in the catalytic cycle.

General Procedure for the Silylation and Borylation of Aryl Fluorides:

Procedure for the silylation of aryl fluorides: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with Fe(OAc)$_2$ (3.5 mg, 0.02 mmol, 0.1 equiv), P(m-tol)$_3$ (12 mg, 0.04 mmol, 0.2 equiv), t-BuONa (48.1 mg, 0.5 mmol, 2.5 equiv) in glove box. Aryl Fluorides (0.2 mmol), fresh distilled silylborane **2aa** (4.0 equiv), fresh distilled cyclohexane (0.8 mL) were then added under nitrogen atmosphere. The reaction mixture was allowed to stir at 135 °C in oil bath for 12 h. The cooled solution was quenched with saturated NH$_4$Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel chromatography to afford the corresponding compound.

Procedure for the borylation of aryl fluorides: A 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar was charged with Fe(acac)$_3$ (10.6 mg, 0.03 mmol, 0.1 equiv), SIMes·HCl (5.3 mg, 0.015 mmol, 0.05 equiv), t-BuONa (115.4 mg, 1.2 mmol, 4.0 equiv) in glove box. Aryl Fluorides (0.3 mmol), Bis(pinacolato)diboron **2b** (228.5 mg, 3.0 equiv), fresh distilled dioxane (2.0 mL) were then added under nitrogen atmosphere. The reaction mixture was allowed to stir at 130 °C in oil bath for 12 h. The cooled solution was quenched with saturated NH$_4$Cl aqueous solution, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel chromatography to afford the corresponding compound.

Other unsuccessful aryl fluorides:
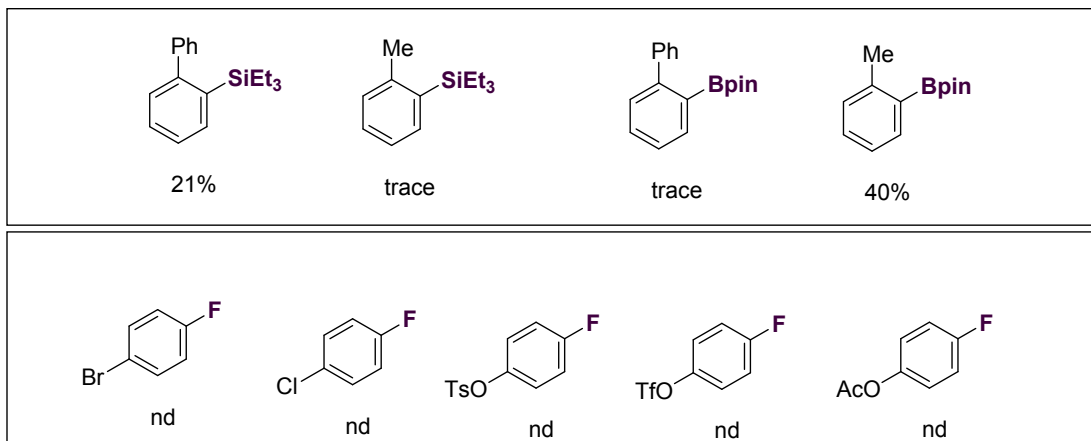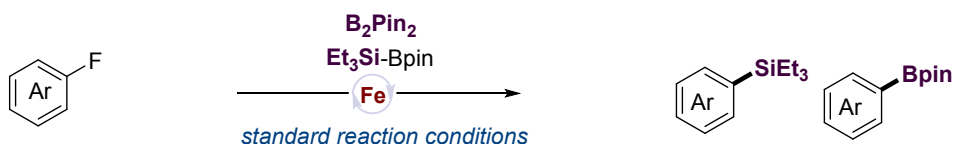
Characterization Data for Products.
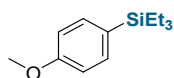
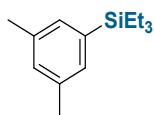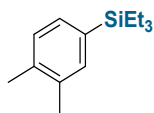**Triethyl(4-methoxyphenyl)silane (1).** This compound is known[3]. The product **1** (33.3 mg, 75% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 8.0 Hz, 2 H), 6.93 (d, J = 8.0 Hz, 2 H), 3.82 (s, 3 H), 0.97 (t, J = 7.9 Hz, 9 H), 0.78 (q, J = 7.9 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.3, 135.7, 128.3, 113.6, 55.1, 7.6, 3.6.
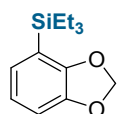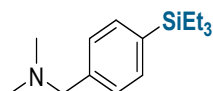

Benzo[d][1,3]dioxol-4-yltriethylsilane (2). This compound is unknown. The product **2** (33 mg, 70% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.86-6.81 (m, 3 H), 5.90 (s, 2 H), 0.97 (t, J = 7.6 Hz, 9 H), 0.82 (q, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.5, 146.0, 127.3, 121.3, 116.9, 109.3, 100.0, 7.5, 3.4. FTMS (EI): Calculated for C$_{13}$H$_{20}$O2Si [M]$^+$: 236.12271; Found: 236.12272.
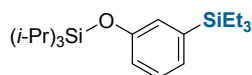
triethyl(3-((triisopropylsilyl)oxy)phenyl)silane (3). This compound is unknown. The product **3** (44.4 mg, 61% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 (t, J = 7.6 Hz, 1 H), 7.05 (d, J = 7.2 Hz, 1 H), 7.02 (s, 1 H), 6.88 (m, 1 H), 1.33-1.19 (m, 3 H), 1.11 (d, J = 7.4 Hz, 18 H), 0.96 (t, J = 7.9 Hz, 9 H), 0.78 (q, J = 7.9 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.6, 139.0, 128.9, 126.9, 125.6, 120.6, 18.1, 12.9, 7.5, 3.5. FTMS (EI): Calculated for C$_{13}$H$_{20}$O2Si (M-C$_3$H$_7$)$^+$: 321.2070; Found: 321.2063.
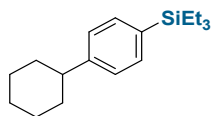
(4-Cyclohexylphenyl)triethylsilane (4). This compound is known[10]. The product **4** (41.6 mg, 76% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 2.50 (m, 1 H), 1.95-1.81 (m, 4 H), 1.80-1.73 (m, 1 H), 1.50-1.35 (m, 5 H), 0.98 (t, J = 7.6 Hz, 9 H), 0.80 (q, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.7, 134.4, 126.4, 44.6, 34.5, 27.1, 26.3, 7.6, 3.6.
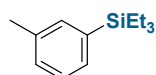
Triethyl(*m*-tolyl)silane (5). This compound is known[2]. The product **5** (34.2 mg, 0.2 mmol, 83% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.29 (m, 2 H), 7.29-7.23 (m, 1 H), 7.22-7.15 (m, 1 H), 2.38 (s, 3 H), 0.99 (t, J = 7.8 Hz, 9 H), 0.80 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.3, 136.9, 134.9, 131.2, 129.5, 127.6, 21.6, 7.4, 3.4.
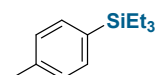
Triethyl(*p*-tolyl)silane (6). This compound is known[3]. The product **6** (29.3 mg, 0.2 mmol, 71% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 7.6 Hz, 2 H), 7.18 (d, J = 7.6 Hz, 2 H), 2.36 (s,

3 H), 0.96 (t, J = 7.9 Hz, 9 H), 0.78 (q, J = 7.9 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.6, 134.4, 133.8, 128.7, 21.6, 7.6, 3.5.

(3,5-Dimethylphenyl)triethylsilane (7). This compound is known[10]. The product **7** (33.9 mg, 77% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09 (s, 2 H), 7.00 (s, 1 H), 2.32 (s, 6 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.78 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.3, 137.0, 132.0, 130.7, 21.6, 7.6, 3.5.
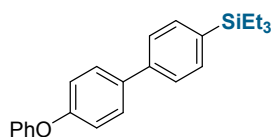

3,4-Dimethyl-1-(triethylsilyl)benzene (8). This compound is known[2]. The product **8** (28.6 mg, 65% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25-7.22 (m, 2 H), 7.13 (d, J = 7.2 Hz, 1 H), 2.27 (s, 3 H), 2.26 (s, 3 H), 0.96 (t, J = 7.8 Hz, 9 H), 0.77 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.4, 135.9, 135.6, 134.4, 132.0, 129.2, 29.9, 19.9, 7.6, 3.5.
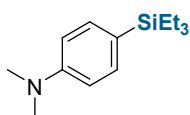
N, N-dimethyl-4-(triethylsilyl)aniline (9). This compound is known[2]. The product **9** (30.5 mg, 65% yield) as a yellow oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, J = 8.4 Hz, 2 H), 6.75 (d, J = 8.4 Hz, 2 H), 2.97 (s, 6 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.76 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.9, 135.4, 122.4, 112.0, 40.3, 7.7, 3.7.
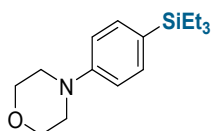
4-(4-(triethylsilyl)phenyl)morpholine (10). This compound is known[7]. The product **10** (44.3 mg, 80% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, J = 7.4 Hz, 2 H) 6.91 (d, J = 7.4 Hz, 2 H), 4.03-3.62 (m, 4 H), 3.37-2.91 (m, 4 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.77 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.6, 135.5, 127.0, 114.8, 67.1, 48.8, 7.6, 3.7.

**N,N-dimethyl-1-(4-(triethylsilyl)phenyl)methanamine (11).** The product **11** (38.3 mg, 77% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, J = 7.6 Hz, 2 H) 7.32 (d, J = 7.6 Hz, 2 H), 3.55 (s, 2 H), 2.34 (s, 6 H), 0.96 (t, J = 7.8 Hz, 9 H), 0.87-0.74 (m, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.6, 136.4, 134.4, 128.7, 64.3, 45.3, 7.5, 3.5.
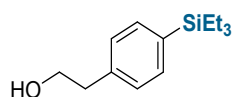
2-(4-(triethylsilyl)phenyl)ethan-1-ol (12). This compound is unknown. The product **12** (16.5 mg, 35% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, J = 7.6 Hz, 2 H), δ 7.22 (d, J = 7.6 Hz, 2 H), 3.88 (t, J = 6.8 Hz, 2 H), 2.87 (t, J = 6.8 Hz, 2 H), 0.96 (t, J = 7.8 Hz, 9 H), 0.78 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.0, 135.4, 134.7, 128.6, 63.7, 39.3, 7.6, 3.5. FTMS (EI): Calculated for C$_{12}$H$_{19}$OSi (M-C$_2$H$_5$)$^+$: 207.11997; Found: 207.11959.
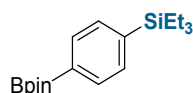
triethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (13). This compound is known[1]. The product **13** (41.3 mg, 65% yield) as a yellow solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, J = 7.6 Hz, 2 H), 7.50 (d, J = 7.6 Hz, 2 H), 1.34 (s, 12 H), 0.95 (t, J = 7.6 Hz, 9 H), 0.79 (q, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.4, 133.9, 133.7, 83.9, 25.0, 7.5, 3.4.
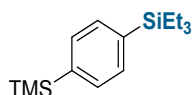
triethyl(4-(trimethylsilyl)phenyl)silane (14). This compound is known[11]. The product **14** (38 mg, 72% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53-7.48 (m, 4 H), 0.98 (t, J = 7.8 Hz, 9 H), 0.80 (q, J = 7.8 Hz, 6 H), 0.28 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.9, 138.1, 133.6, 132.7, 7.6, 3.5, 1.0.
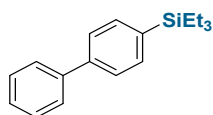
[1,1'-biphenyl]-4-yltriethylsilane (15). This compound is known[2]. The product **15** (45.6 mg, 85% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64-7.57 (m, 6 H), 7.45 (t, J = 7.6 Hz, 2 H), 7.36 (t, J = 7.2 Hz, 1 H), 1.02 (t, J = 7.8 Hz, 9 H), 0.84 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.5, 141.3, 136.3, 134.8, 128.9, 127.4, 127.3, 126.5, 7.6, 3.5.
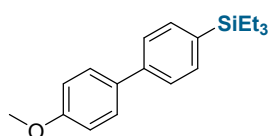
Triethyl(4'-methoxy-[1,1'-biphenyl]-4-yl)silane (16). This compound is known[5]. The product **16** (57.8 mg, 97% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59-7.51 (m, 6 H), 7.03 – 6.92 (m, 2 H), 3.86 (s, 3 H), 1.00 (t, J = 7.8 Hz, 9 H), 0.82 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.3, 141.1, 135.6, 134.8, 133.8, 128.3, 126.1, 114.3, 55.5, 7.6, 3.5.

Triethyl(4'-phenoxy-[1,1'-biphenyl]-4-yl)silane (17). This compound is known[7]. The

product **17** (39.6 mg, 55% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60-7.58 (m, 6 H), 7.38 (m, 2 H), 7.14 (m, 1 H), 7.11-7.08 (m, 4 H), 1.02 (t, J = 7.8 Hz, 9 H), 0.85 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.2, 157.0, 140.8, 136.3, 136.1, 134.9, 129.9, 128.5, 126.3, 123.5, 119.2, 119.1, 7.6, 3.5.
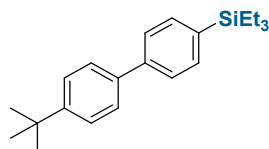
(4'-(Tert-butyl)-[1,1'-biphenyl]-4-yl)triethylsilane (18). This compound is known[4]. The product **18** (59.6 mg, 92% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60-7.56 (m, 6 H), 7.49-7.46 (m, 2 H), 1.39 (s, 9 H), 1.02 (t, J = 7.8 Hz, 9 H), 0.85 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.4, 141.4, 138.4, 136.0, 134.8, 126.9, 126.4, 125.8, 34.7, 31.5, 7.6, 3.6.
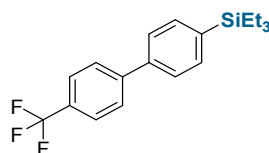
Triethyl(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)silane (19). This compound is known[7]. The product **19** (28.2 mg, 42% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73-7.68 (m, 4 H), 7.62-7.57 (m, 4 H), 1.00 (t, J = 7.6 Hz, 9 H), 0.83 (q, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.8, 138.9 (q, J_{CF} = 228.0 Hz), 135.0, 129.5 (q, J_{CF} = 32.0 Hz), 127.5, 126.5, 125.8 (q, J_{CF} = 4.0 Hz), 123.1, 7.6, 3.5.
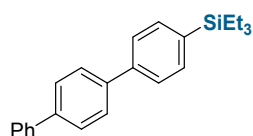
[1,1':4',1''-terphenyl]-4-yltriethylsilane (20). This compound is unknown. The product **20** (42.7 mg, 62% yield) as a white solid was purified with silica gel

chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (s, 4 H), 7.67-7.61 (m, 4 H), 7.59-7.55 (m, 2 H), 7.47-7.42 (m, 2 H), 7.40-7.36 (m, 1 H), 1.00 (t, J = 7.8 Hz, 9 H), 0.83 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.1, 141.0, 140.8, 140.2, 140.2, 136.5, 134.9, 129.0, 127.6, 127.5, 127.2, 126.4, 7.6, 3.5. FTMS (EI): Calculated for C$_{24}$H$_{28}$Si (M)$^+$: 344.19548; Found: 344.19459.
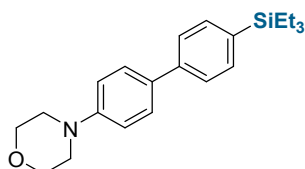
4-(4'-(triethylsilyl)-[1,1'-biphenyl]-4-yl)morpholine (21). This compound is known[5]. The product **21** (42.4 mg, 60% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60-7.50 (m, 6 H), 6.99 (d, J = 8.4 Hz, 2 H), 3.93-3.84 (m, 4 H), 3.27-3.18 (m, 4 H), 1.01 (t, J = 7.8 Hz, 9 H), 0.83 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.6, 141.1, 135.4, 134.8, 132.7, 127.9, 125.9, 115.8, 67.0, 49.2, 7.6, 3.5.
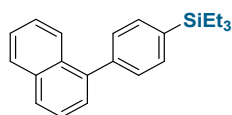
Triethyl(4-(naphthalen-1-yl)phenyl)silane (22). This compound is known[10]. The product **22** (40.7 mg, 64% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 8.4 Hz, 1 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.88 (d, J = 8.4 Hz, 1 H), 7.64-7.62 (m, 2 H), 7.57-7.44 (m, 6 H), 1.07 (t, J = 7.8 Hz, 9 H), 0.89 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.1, 140.4, 136.3, 134.3, 133.9, 131.7, 130.2, 129.5, 128.4, 127.7, 127.1, 126.3, 126.2, 126.1, 125.9, 125.5, 7.7, 3.6.
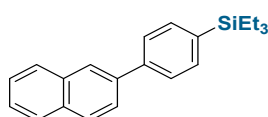
Triethyl(4-(naphthalen-2-yl)phenyl)silane (23). This compound is known[6]. The

product **23** (38.2 mg, 60% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (s, 1 H), 7.95-7.87 (m, 3 H), 7.80-7.76 (m, 1 H), 7.76-7.70 (m, 2 H), 7.66-7.60 (m, 2 H), 7.55-7.45 (m, 2 H), 1.03 (t, J = 8.0 Hz, 9 H), 0.86 (q, J = 8.0 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.4, 138.6, 136.5, 134.9, 133.8, 132.8, 128.5, 128.4, 127.8, 126.8, 126.4, 126.1, 125.9, 125.7, 7.6, 3.6.
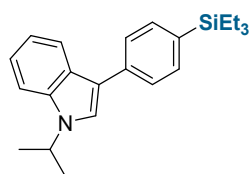
1-isopropyl-3-(4-(triethylsilyl)phenyl)-1H-indole (24). This compound is unknown. The product **24** (50 mg, 72% yield) as a white solid w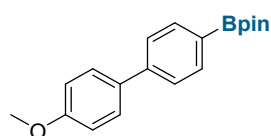as purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J = 8.0 Hz, 1 H), 7.68 (d, J = 7.6 Hz, 2 H), 7.58 (d, J = 7.6 Hz, 2 H), 7.44 (d, J = 6.0 Hz, 2 H), 7.28 (t, J = 7.8 Hz, 1 H), 7.20 (t, J = 7.4 Hz, 1 H), 4.73 (p, J = 6.8 Hz, 1 H), 1.59 (d, J = 6.8 Hz, 6 H), 1.03 (t, J = 7.8 Hz, 9 H), 0.82-0.88 (m, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.5, 136.5, 134.8, 134.2, 126.7, 126.3, 121.8, 121.8, 120.3, 120.0, 117.0, 109.9, 47.2, 25.2, 23.0, 7.6, 3.6. FTMS (EI): Calculated for C$_{23}$H$_{31}$NSi (M)$^+$: 349.22203; Found: 349.22165.
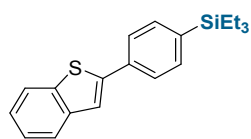
(4-(benzo[b]thiophen-2-yl)phenyl)triethylsilane (25). This compound is unknown. The product **25** (53 mg, 81% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 8.0 Hz,1 H), 7.79 (d, J = 7.6 Hz, 1 H), 7.72 (d, J = 7.6 Hz, 2 H), 7.59 (d, J = 4.8 Hz, 2 H), 7.56 (s, 1 H), 7.35 (m, 2 H), 1.01 (t, J = 7.8 Hz, 9 H), 0.84 (q, J = 7.9 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.5, 140.8, 139.6, 138.0, 134.9, 134.6, 125.7, 124.6, 124.4, 123.7, 122.4, 119.5, 7.6, 3.4. FTMS (EI): Calculated for C$_{20}$H$_{24}$SSi (M)$^+$: 324.13625; Found: 324.13630.
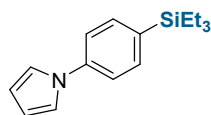
1-(4-(triethylsilyl)phenyl)-1H-pyrrole (26). This compound is known[5]. The product **26** (36 mg, 71% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.12 (s, 2 H), 6.35 (s, 2 H), 1.00(t, J = 7.8 Hz, 9 H), 0.83 (q, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.2, 135.6, 134.6, 119.8, 119.3, 110.5, 7.5, 3.5.
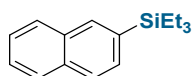
triethyl(naphthalen-2-yl)silane (27). This compound is known[10]. The product **27** (32 mg, 66% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (s, 1 H), 7.90-7.76 (m, 3 H), 7.67-7.57 (m, 1 H), 7.50 (m, 2 H), 1.03 (t, J = 7.6 Hz, 9 H), 0.90 (q, J = 7.7 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl3): δ 135.1, 134.9, 133.8, 133.1, 130.7, 128.1, 127.8, 126.9, 126.3, 125.9, 7.6, 3.5.
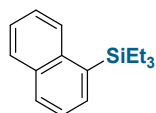
Triethyl(naphthalen-1-yl)silane (28). This compound is known[10]. The product **28** (34 mg, 70% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16-8.13 (m, 1 H), 7.90-7.88 (m, 2 H), 7.69 (d, J = 6.8 Hz, 1 H), 7.55-7.47 (m, 3 H), 1.10-0.97 (m, 15 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.6, 135.3, 134.6, 133.5, 129.7, 129.2, 128.0, 125.7, 125.4, 125.2, 7.8, 4.6.
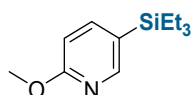
2-methoxy-5-(triethylsilyl)pyridine (29). This compound is known[7]. The product **29** (25.9 mg, 58% yield) as a yellow oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (s, 1 H), 7.63 (d, J = 8.4 Hz, 1 H), 6.74 (d, J = 8.4 Hz, 1 H), 3.94 (s, 3 H), 0.96 (t, J = 7.8 Hz, 9 H), 0.77 (q, J = 7.8 Hz, 6 H). ^{13}C NMR (100

MHz, CDCl$_3$) δ 164.8, 152.4, 144.3, 123.3, 110.8, 53.3, 7.4, 3.4.
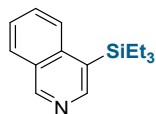
4-(triethylsilyl)isoquinoline (30). This compound is unknown. The product **30** (25 mg, 51% yield) as a yellow oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.24 (s, 1 H), 8.57 (s, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.70 (t, J = 7.6 Hz, 1 H), 7.60 (m, J = 7.4 Hz, 1 H), 1.07-0.86 (m, 15 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.1, 149.7, 140.0, 130.3, 129.0, 128.3, 126.8, 126.8, 7.7, 4.3. FTMS (EI): Calculated for C$_{15}$H$_{21}$NSi (M)$^+$: 243.14378; Found: 243.14381.
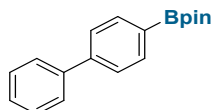
2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31).
This compound is known[8]. The product **31** (59.6 mg, 0.3 mmol, 71% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, J = 7.2 Hz, 2 H), 7.66 (d, J = 7.2 Hz, 4 H), 7.47 (t, J = 7.2 Hz, 2 H), 7.39 (t, J = 7.2 Hz, 1 H), 1.34 (s, 12 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.0, 141.1, 135.4, 128.9, 127.7, 127.3, 126.6, 83.9, 25.0.
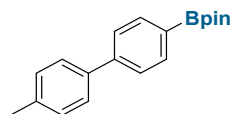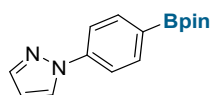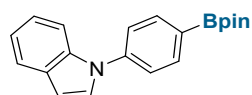

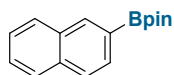**4-Methyl-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (32).** This compound is known[12]. The product **32** (54.7 mg, 0.3 mmol, 62% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, J = 7.8 Hz, 2 H), 7.62 (d, J = 7.8 Hz, 2 H), 7.54 (d, J = 7.8 Hz, 2 H), 7.27 (d, J = 7.8 Hz, 2 H), 2.41 (s, 3 H), 1.38 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.0, 138.2, 137.5, 135.4 , 129.6 , 127.2 , 126.4 , 83.9 , 25.0 , 21.2.
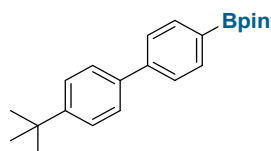
2-(4'-(Tert-Butyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33). This compound is known[8]. The product **33** (55.4 mg, 0.3 mmol, 55% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, J = 7.6 Hz, 2 H), 7.61 (d, J = 8.0 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 1.37 (s, 21 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.8, 143.9, 138.2, 135.4, 127.0, 126.4, 125.9, 83.9, 34.7, 31.5, 25.0.


2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34). This compound is known[9]. The product **34** (56.7 mg, 0.3 mmol, 61% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, J = 8.0 Hz, 2 H), 7.72-7.50 (m, 4 H), 6.98 (d, J = 8.8 Hz, 2 H), 3.85 (s, 3 H), 1.37 (s, 12 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.5, 143.6, 135.4, 133.6, 128.4, 126.1, 114.4, 83.9, 55.5, 25.0.
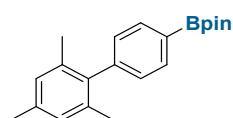
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2′,4′,6′-trimethylbiphenyl (35). This compound is known[12]. The product **35** (43.5 mg, 0.3 mmol, 45% yield) as a colorless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J = 7.6 Hz, 2 H), 7.17 (d, J = 7.6 Hz, 2 H), 6.95 (s, 2 H), 2.34 (s, 3 H), 2.00 (s, 6 H), 1.39 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.4, 139.0, 136.7, 135.8, 135.0, 128.9, 128.2, 83.9, 25.0, 21.1, 20.8.
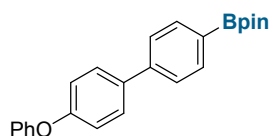
4-Phenoxy-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (36). This compound is known[12]. The product **36** (58 mg, 0.3 mmol, 52% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J=$ 7.6 Hz, 2 H), 7.59 (d, $J = 8.4$ Hz, 4 H), 7.37 (t, $J = 7.8$ Hz, 2 H), 7.14 (t, $J = 7.4$ Hz, 1 H), 7.08 (t, $J = 7.6$ Hz, 4 H), 1.37 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.2, 157.2, 143.3, 136.1, 135.4,135.4, 129.9, 128.7, 126.3, 123.6, 119.2, 84.0, 25.0.
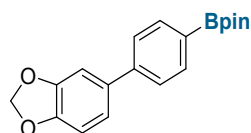
3,4-Methylenedioxy-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (37).

This compound is known[12]. The product **37** (59.3 mg, 0.3 mmol, 61% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (CDCl$_3$) δ 7.86 (d, $J = 7.6$ Hz, 2 H), 7.54 (d, $J = 8.0$ Hz, 2 H), 7.10-7.08 (m, 2 H), 6.88 (m, 1 H), 6.00 (s, 2 H), 1.37 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.3, 147.4, 143.7, 135.4, 126.3, 120.9, 108.7, 107.8, 101.3, 83.9, 25.0.
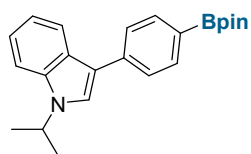
1-Isopropyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)indole (38). This compound is known[12]. The product **38** (49.8 mg, 0.3 mmol, 46% yield) as a pale yellow oil was purified with silica gel chromatography. ^{1}H NMR (CDCl$_3$) δ 7.99 (d, $J = 8.0$ Hz, 1 H), 7.90 (d, $J = 8.0$ Hz, 2 H), 7.71 (d, $J = 8.0$ Hz, 2 H), 7.46 (s, 1 H), 7.44 (d, $J = 8.4$ Hz, 1 H), 7.28 (d, $J = 7.5$ Hz, 1 H), 7.20 (d, $J = 7.5$ Hz, 1 H), 4.73 (m, 1 H), 1.59 (d, $J = 6.8$ Hz, 6 H), 1.39 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.0, 136.6, 135.4, 126.5 , 126.2, 122.1, 121.9, 120.2, 116.8, 109.9, 83.8 , 47.3, 25.0 , 23.0.
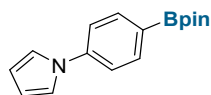
N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrole (39).
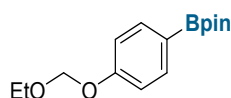
This compound is known[12]. The product **39** (46.8 mg, 0.3 mmol, 58% yield) as a colorless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2 H), 7.15-7.14 (m, 2 H), 6.36-6.35 (m, 2 H), 1.36 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.9, 136.4, 119.4, 119.2, 110.9, 84.0, 25.0.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-pyrazole (40). This compound is known[12]. The product **40** (44.6 mg, 0.3 mmol, 55% yield) as a colorless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (m, 1 H), 7.88 (d, J = 8.1 Hz, 2 H), 7.75-7.70 (m, 2 H), 7.74 (s, 1 H), 6.48 (m, 1 H), 1.36 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.3, 141.5, 136.3, 126.9, 118.1, 108.0, 84.1, 25.0.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-Indole (41). This compound is unknown. The product **41** (55.5 mg, 0.3 mmol, 58% yield) as a colorless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 7.6 Hz, 1 H), 7.63 (d, J = 8.4 Hz, 1 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 3.2 Hz, 1 H), 7.17-7.27 (m, 2 H), 6.71 (d, J = 2.8 Hz, 1 H), 1.39 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.4, 136.4, 135.7, 129.7, 128.3, 127.8, 124.7, 123.3, 122.6, 121.3, 120.7, 110.8, 104.2, 84.1, 77.5, 77.2, 76.8, 25.0. FTMS (EI): Calculated for C$_{20}$H$_{10}$BO$_2$ (M)$^+$: 319.17381; Found: 319.17336.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (42). This compound is known[8]. The product **42** (48.8 mg, 0.3 mmol, 64% yield) as a brown solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 1 H), 7.80-7.91 (m, 4 H), 7.44-7.54 (m, 2 H), 1.39 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.4, 135.2, 133.0, 130.5, 128.8, 127.8, 127.1, 125.9, 84.0, 25.1.
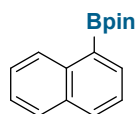
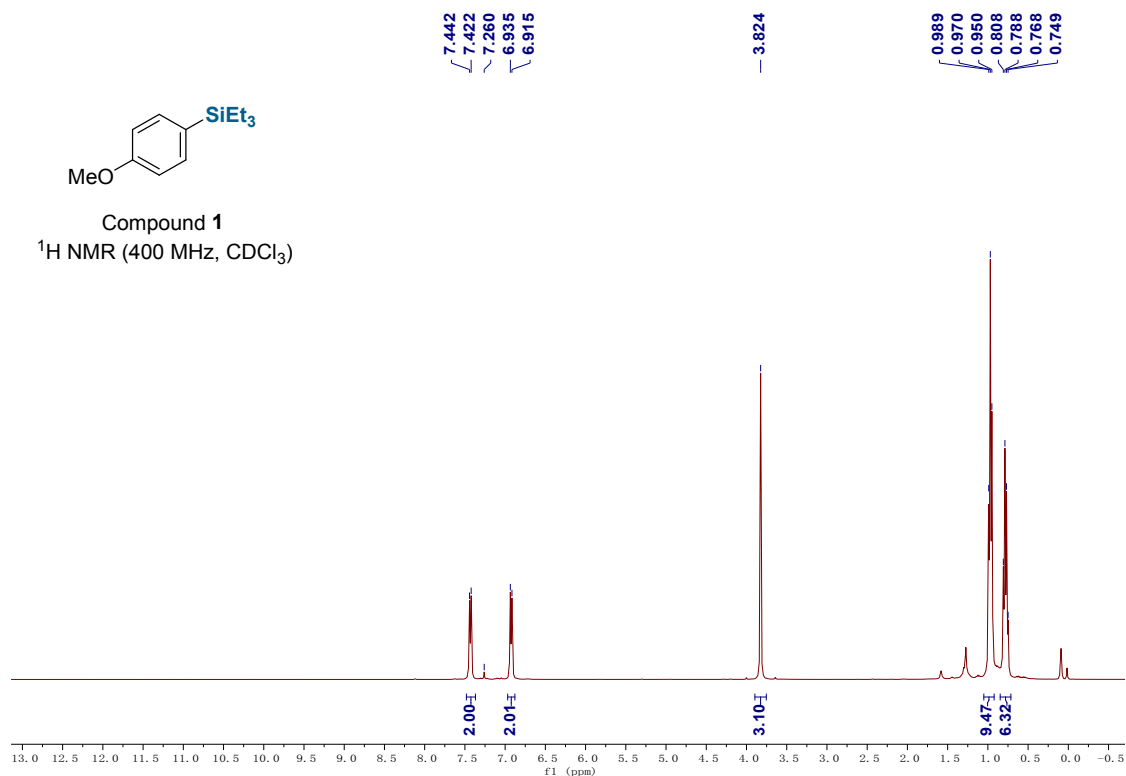**1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (43).** This compound is known[8]. The product **43** (57.9 mg, 0.3 mmol, 76% yield) as a colorless solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.76 (m, 1 H), 8.08 (m, 1 H), 7.93 (m, 1 H), 7.83 (m, 1 H), 7.50-7.56 (m, 1 H), 7.43-7.50 (m, 2 H), 1.43 (s, 12 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.1, 135.8, 133.3, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.8, 25.1.
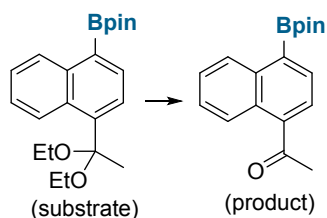
1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)ethan-1-one (44). This compound is known[13]. The product **44** (26.6 mg, 0.3 mmol, 30% yield) as a colorless solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.79 (m, 1 H), 8.56 (m, 1 H), 8.07 (d, J = 7.2 Hz, 1 H), 7.81 (d, J = 7.2 Hz, 1 H), 7.57 (m, 2 H), 2.74 (s, 3 H) 1.44 (s, 12 H).
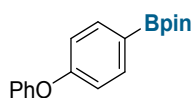
4,4,5,5-Tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane (45). This

compound is known[8]. The product **45** (45.3 mg, 0.3 mmol, 51% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, J = 8.4 Hz, 2 H), 7.35 (t, J = 8.4 Hz, 2 H), 7.13 (t, J = 7.4 Hz, 1 H), 7.03 (d, J = 8.4 Hz, 2 H), 6.99 (d, J = 8.4 Hz, 2 H), 1.35 (s, 12 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.3, 156.7, 136.8, 129.9, 123.8, 119.6, 117.8, 83.9, 25.0.
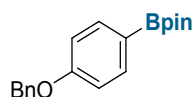
2-(4-(benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane   (46).   This compound is known[14]. The product **46** (60.5 mg, 0.3 mmol, 65% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, J = 8.5 Hz, 2 H), 7.45-7.29 (m, 5 H), 6.98 (d, J = 8.5 Hz, 2 H), 5.09 (s, 2 H), 1.33 (s, 12 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.5, 137.0, 136.7, 128.7, 128.1, 127.6, 114.4, 83.7, 69.9, 25.0.
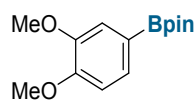
2-(3,4-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane   (47).   This compound is known[9]. The product **47** (40.8 mg, 0.3 mmol, 51% yield) was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, J = 7.6 Hz, 1 H), 7.29 (s, 1 H), 6.88 (d, J = 7.6 Hz, 1 H), 3.92 (s, 3 H), 3.90 (s, 3 H), 1.34 (s, 12 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ151.8, 148.5, 128.7, 116.7, 110.6, 83.8, 56.0, 55.9, 25.0.

2-(4-(ethoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48). The product **48** (50.9 mg, 0.3 mmol, 61% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, J = 8.5 Hz, 2 H), 7.03 (d, J = 8.5 Hz, 2 H), 5.25 (s, 2 H), 3.72 (q, J = 7.1 Hz, 2 H), 1.33 (s, 12 H), 1.21 (t, J = 7.1

Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.1, 136.6, 115.5, 92.9, 83.7, 64.4, 25.0, 15.2.
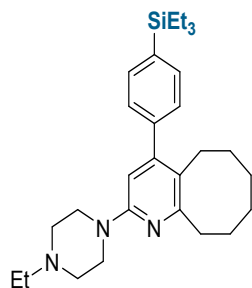
2-(4-ethylpiperazin-1-yl)-4-(4-(triethylsilyl)phenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine (49). This compound is known[5]. The product **49** (57.4 mg, 0.2 mmol, 62% yield) was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, J = 7.6 Hz, 2 H), 7.23 (d, J = 7.6 Hz, 2 H), 6.34 (s, 1 H), 3.55-3.51 (m, 4 H), 2.91-2.87 (m, 2 H), 2.62-2.58 (m, 2 H), 2.57-2.54 (m, 4 H), 2.46 (q, J = 7.2 Hz, 2 H), 1.82-1.76 (m, 2 H), 1.46-1.39 (m, 4 H), 1.38-1.34 (m, 2 H), 1.13 (t, J = 7.2 Hz, 3 H), 0.99 (t, J = 8.0 Hz, 9 H), 0.81 (q, J = 8.0 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ159.9, 157.4, 151.6, 141.9, 136.3, 133.9, 127.9, 123.1, 106.1, 52.9, 52.6, 45.7, 35.6, 31.8, 30.8, 26.7, 26.6, 26.0, 12.1, 7.6, 3.5.
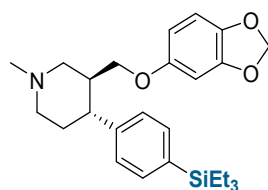
3-((benzo[1,3]dioxol-5-yloxy)methyl)-1-methyl-4-(4-(triethylsilyl)phenyl)piperidine (50). The product **50** (39.5 mg, 0.2 mmol, 45% yield) was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 7.6 Hz, 2 H), 7.18 (d, J = 7.6 Hz, 2 H), 6.61 (d, J = 8.4 Hz, 1 H), 6.34 (s, 1 H), 6.12 (d, J = 8.4 Hz, 1 H), 5.87 (s, 2 H), 3.61-3.57 (m, 1 H), 3.48-3.44 (m, 1 H), 3.27-2.24 (m, 2 H), 3.03-3.00 (m, 2 H), 2.39 (s, 3 H), 0.95 (t, J = 7.6 Hz, 9 H), 0.77 (q, J = 7.6 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.5, 148.2, 144.3, 141.6, 135.6, 134.7, 127.0, 107.9, 105.7, 101.2, 98.1, 69.8, 59.7, 56.3, 46.5, 44.3, 41.7, 34.0, 7.6, 3.5. FTMS (EI): Calculated for C26H37NO3Si (M)$^+$: 439.25427; Found: 439.25268.
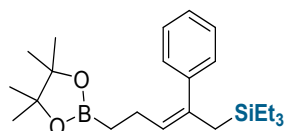
Triethyl(2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)silane

(52). The product **52** (51.8 mg, 67% yield) as a colourless oil was purified with silica gel chromatography. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 -7.27 (m, 2 H), δ 7.27 - 7.23 (m, 2 H), δ 7.20 - 7.16 (m, 1 H), 5.44 (t, J = 6.9 Hz, 1 H), 2.25 (q, J = 7.4 Hz, 2 H), 1.99 (s, 2 H), 1.25 (s, 12 H), 0.93 (t, J = 7.4 Hz, 2 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.36 (q, J = 7.9 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.4, 137.3, 128.5, 128.0, 126.8, 126.4, 83.1, 25.0, 23.8, 16.2, 7.4, 3.9.

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Triethyl(4-methoxyphenyl)silane (1)

Compound **1**
^{1}H NMR (400 MHz, CDCl$_3$)

SiEt₃

MeO

Compound **1**
¹³C NMR (100 MHz, CDCl₃)

160.28 — 135.70 — 128.25 — 113.58 — 77.48 — 77.16 — 76.84 — 55.08 — 7.56 — 3.62

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
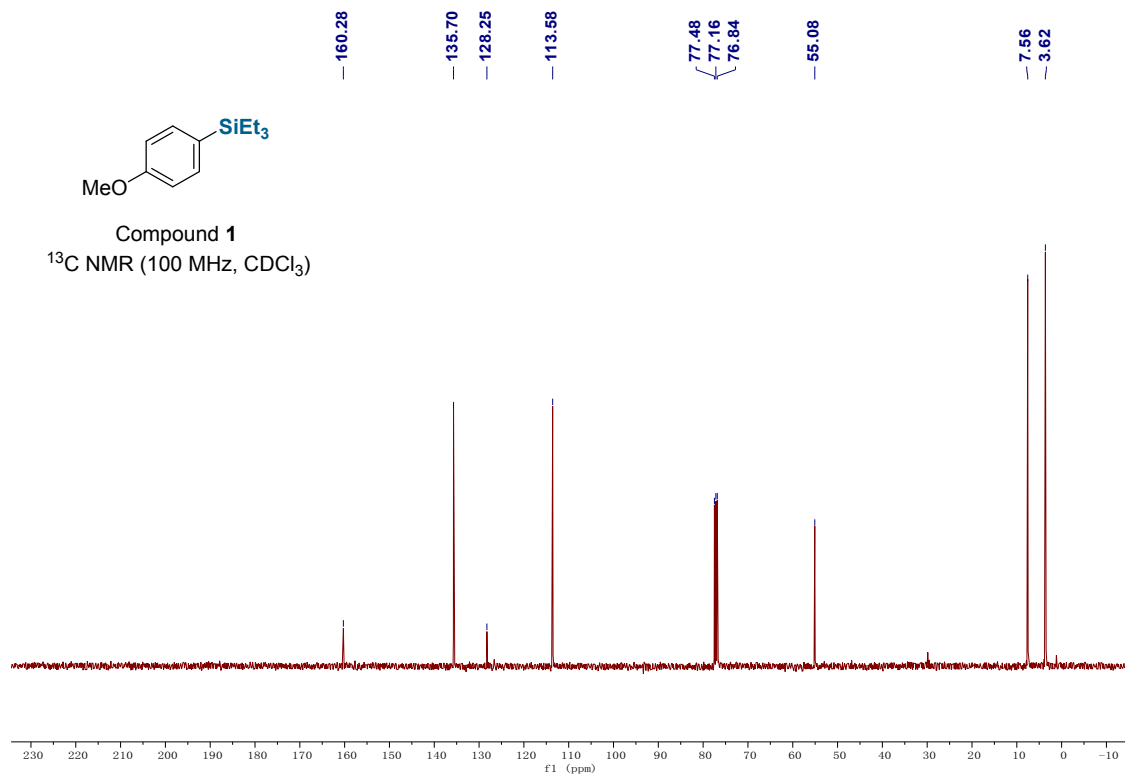
Benzo[d][1,3]dioxol-4-yltriethylsilane (2)
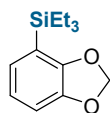
Compound 2

^{1}H NMR (400 MHz, CDCl$_3$)

7.260
6.861
6.855
6.846
6.835
6.823
6.815
6.809
5.901

0.985
0.966
0.947
0.853
0.834
0.815
0.795

3.01 2.02 9.00 6.06

3.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
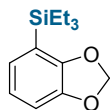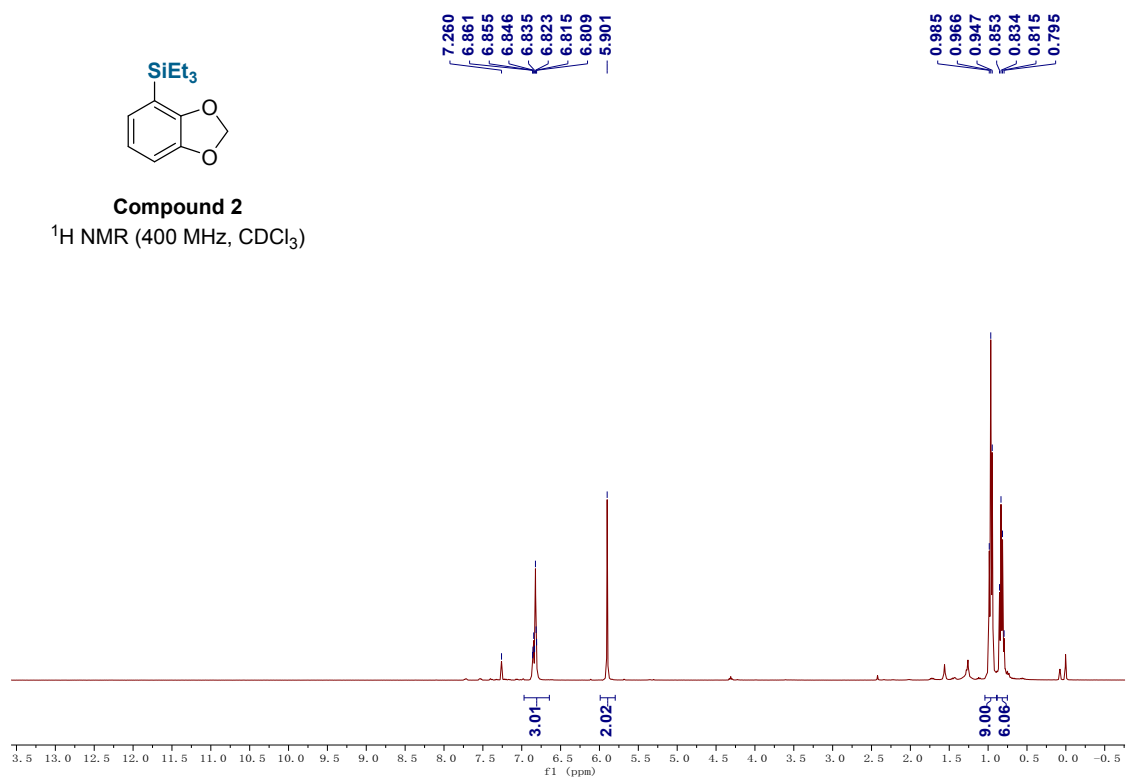
Compound 2

^{13}C NMR (100 MHz, CDCl$_3$)

152.47
146.03
127.33
121.34
116.89
109.34
100.02
77.48
77.16
76.84
7.52
3.37

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

34

Triethyl(3-((triisopropylsilyl)oxy)phenyl)silane (3)

7.260
7.242
7.223
7.204
7.071
7.053
7.029
6.895
6.875

1.314
1.294
1.276
1.261
1.256
1.239
1.222
1.133
1.114
0.994
0.974
0.954
0.816
0.797
0.777
0.757

$(i\text{-Pr})_3\text{Si}$—O— —SiEt_3

Compound 3
^{1}H NMR (400 MHz, CDCl3)

1.07
1.00
1.03
1.03

3.28
18.01
9.06
6.06

f1 (ppm)

155.57

138.95

128.93
126.92
125.56
120.55

77.48
77.16
76.84

18.08
12.88
7.50
3.50

$(i\text{-Pr})_3\text{Si}$—O— —SiEt_3

Compound 3
^{13}C NMR (100 MHz, CDCl3)

f1 (ppm)

35

(4-Cyclohexylphenyl)triethylsilane (4)

Compound 4
^{1}H NMR (400 MHz, CDCl$_3$)
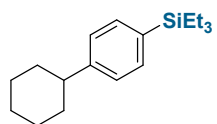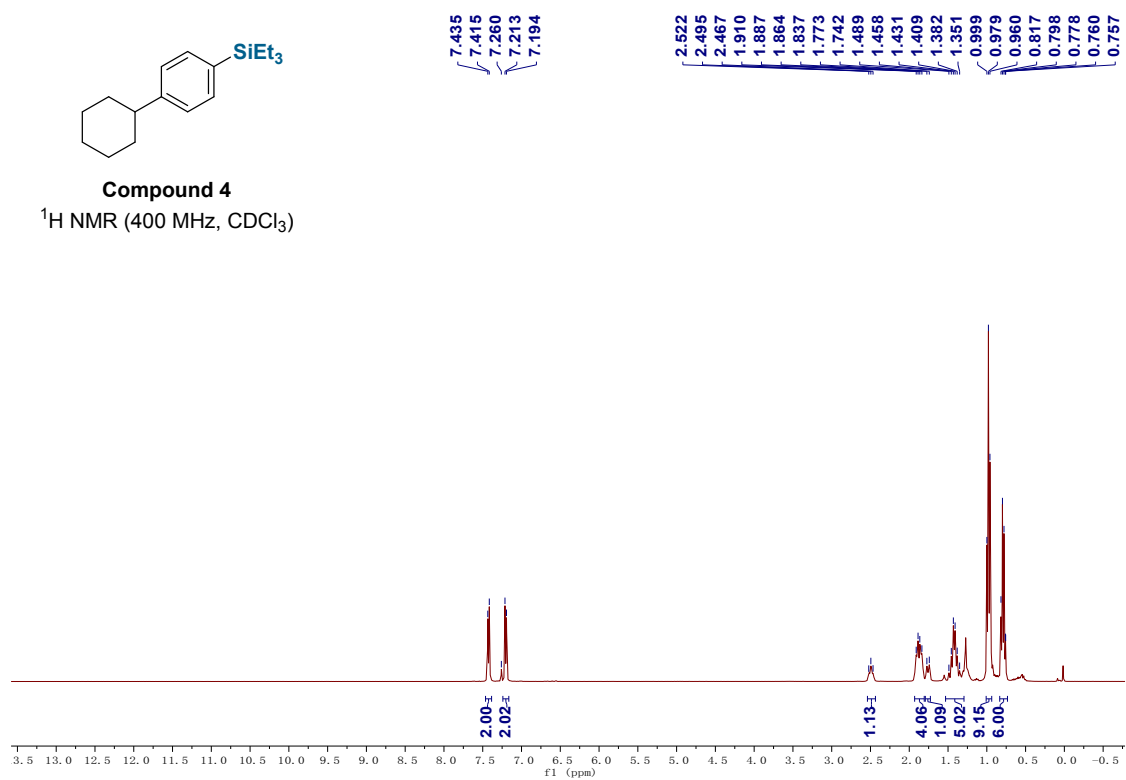
Compound 4
^{13}C NMR (100 MHz, CDCl$_3$)
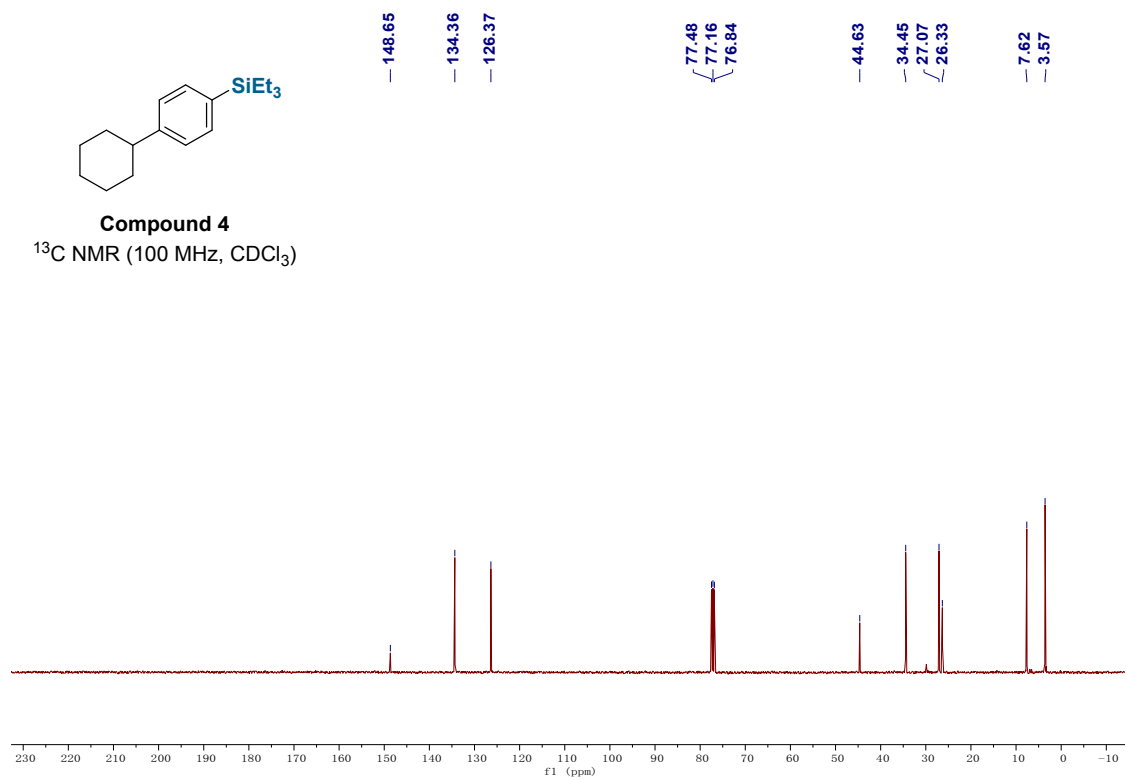
Triethyl(*m*-tolyl)silane (5)
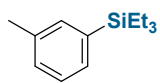
Compound 5
^{1}H NMR (400 MHz, CDCl$_3$)

7.315
7.288
7.269
7.260
7.251
7.198
7.180

2.380

1.010
0.991
0.971
0.838
0.819
0.799
0.779

1.95
0.99
1.03

3.06

9.55
6.33

13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
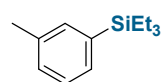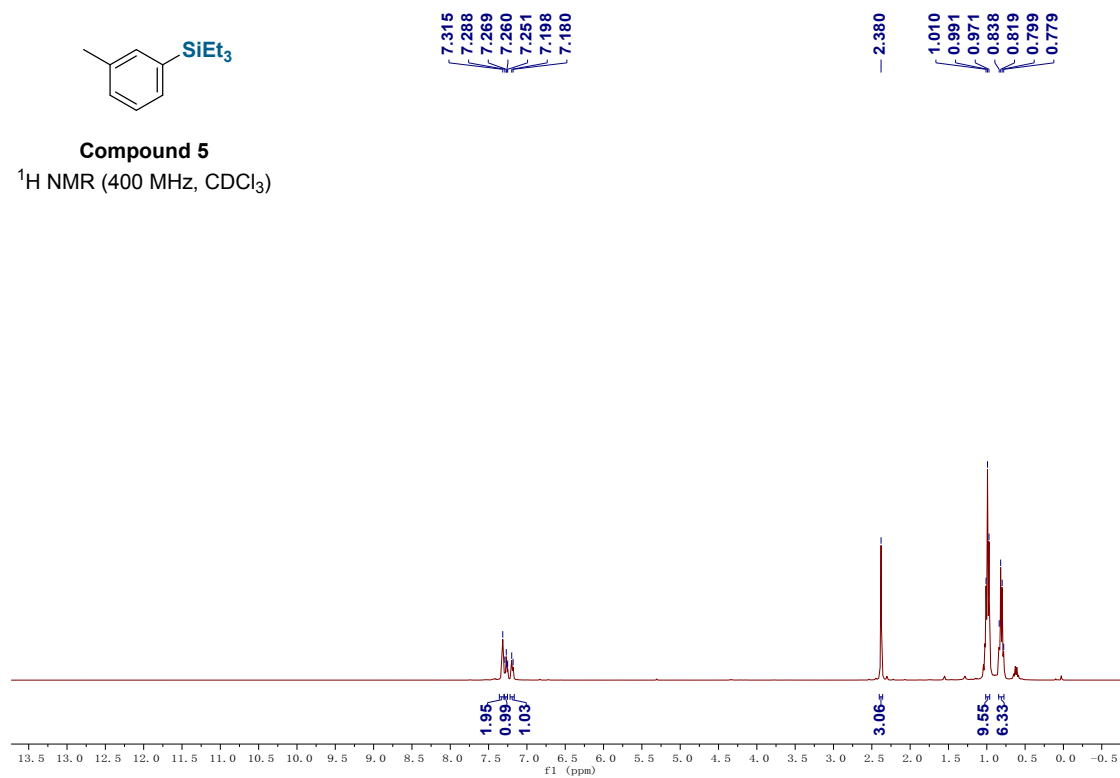
Compound 5
^{13}C NMR (100 MHz, CDCl$_3$)

137.29
136.89
134.83
131.23
129.52
127.55

77.34
77.02
76.71

21.61

7.44
3.35

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

37
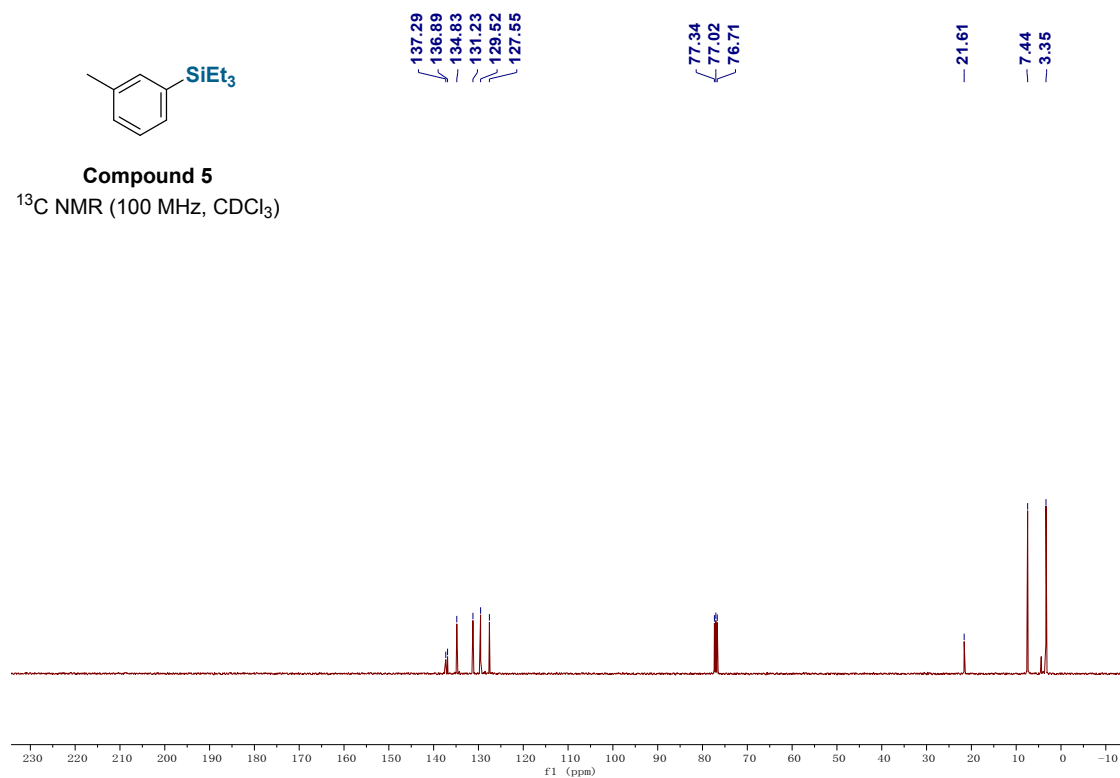
Triethyl(*p*-tolyl)silane (6)
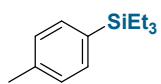
Compound 6
^{1}H NMR (400 MHz, CDCl$_3$)

7.409
7.390
7.260
7.193
7.175

2.356

0.985
0.965
0.946
0.809
0.790
0.771
0.750

1.98
1.97

3.03

9.30
6.15

13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

38
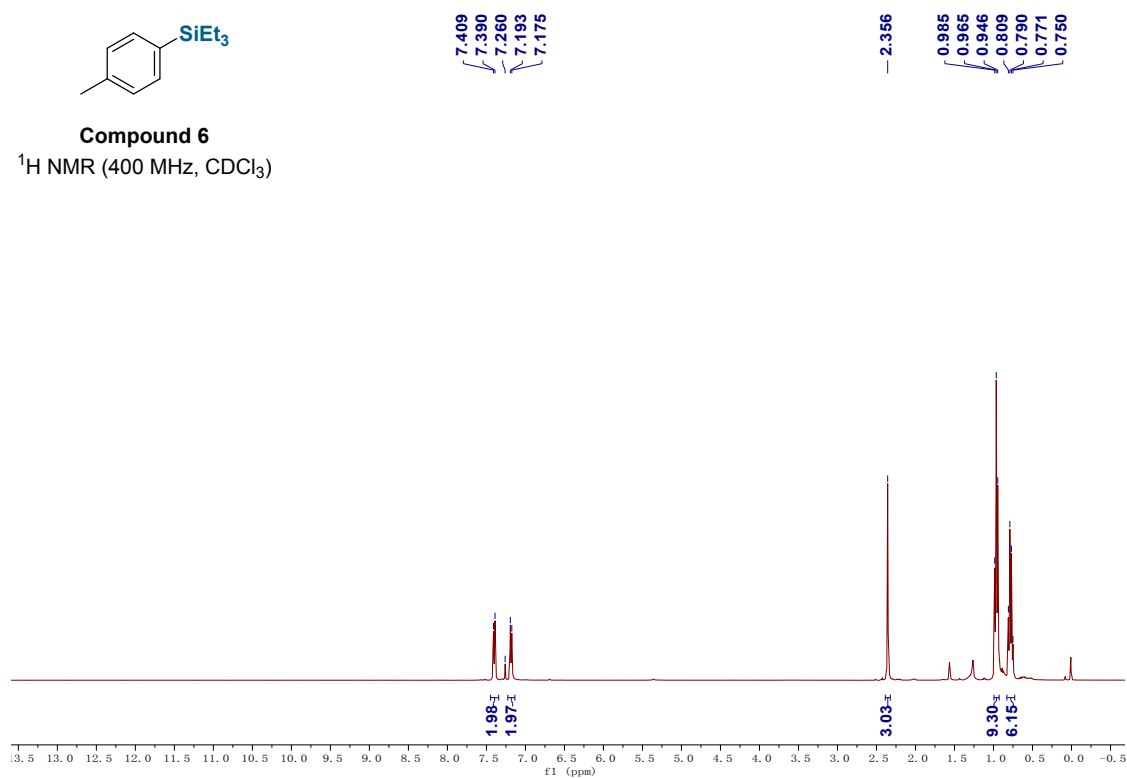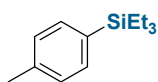
Compound 6

^{13}C NMR (100 MHz, CDCl$_3$)

138.63
134.37
133.81
128.67

77.48
77.16
76.84

21.62

7.57
3.51
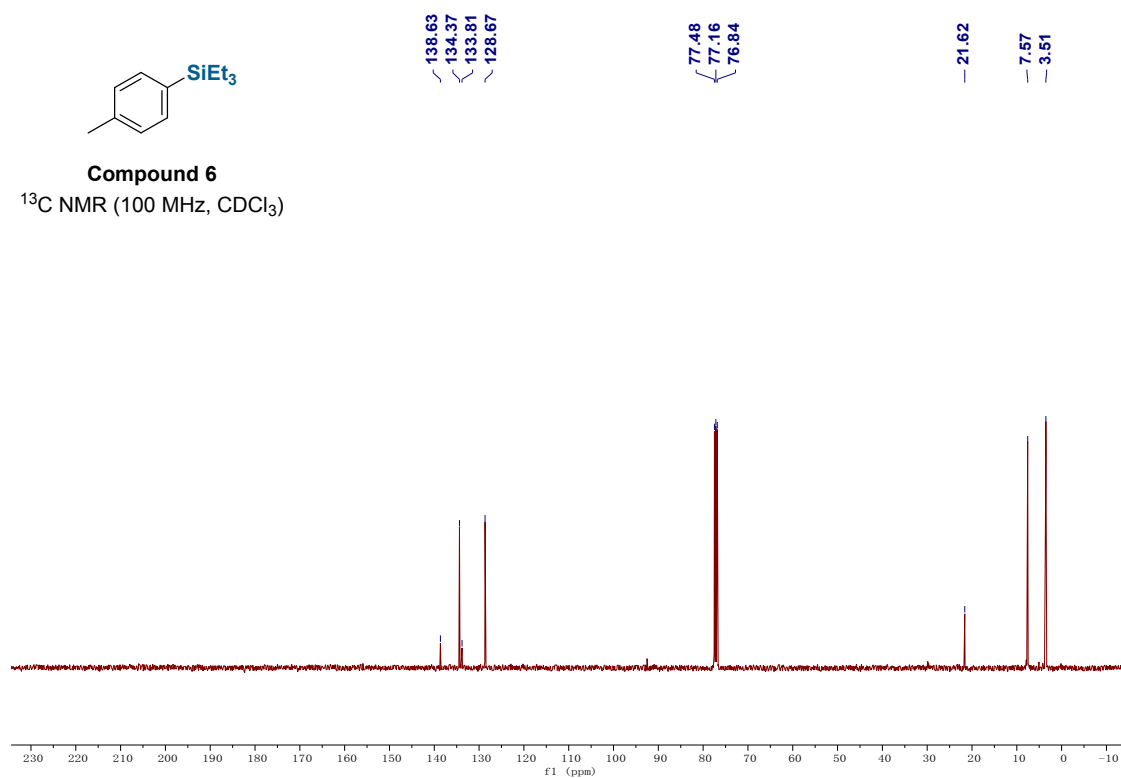
(3,5-Dimethylphenyl)triethylsilane (7)
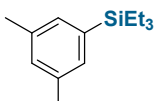
Compound 7

^{1}H NMR (400 MHz, CDCl$_3$)

7.260
7.095
6.997

2.321

0.986
0.967
0.947
0.805
0.785
0.766
0.746

1.96
0.97

6.01

9.29
6.00
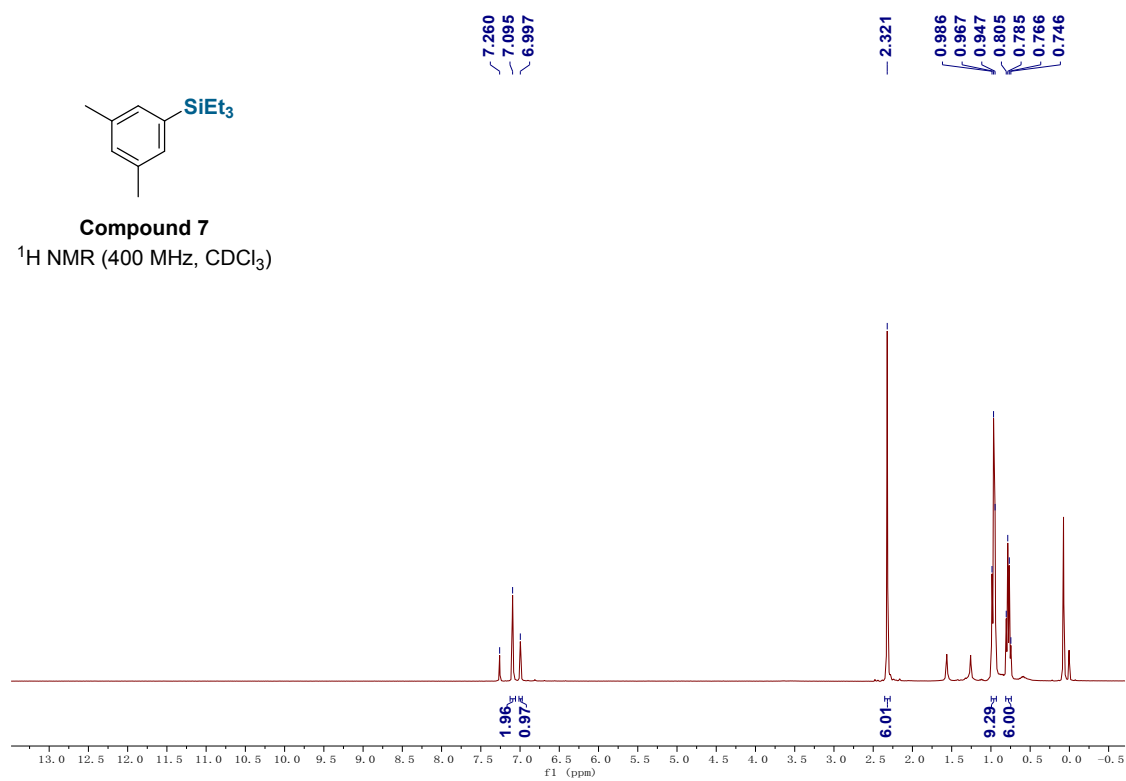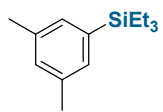
Compound 7
^{13}C NMR (100 MHz, CDCl$_3$)

137.34
136.97
132.02
130.66
77.48
77.16
76.84
21.59
7.62
3.50
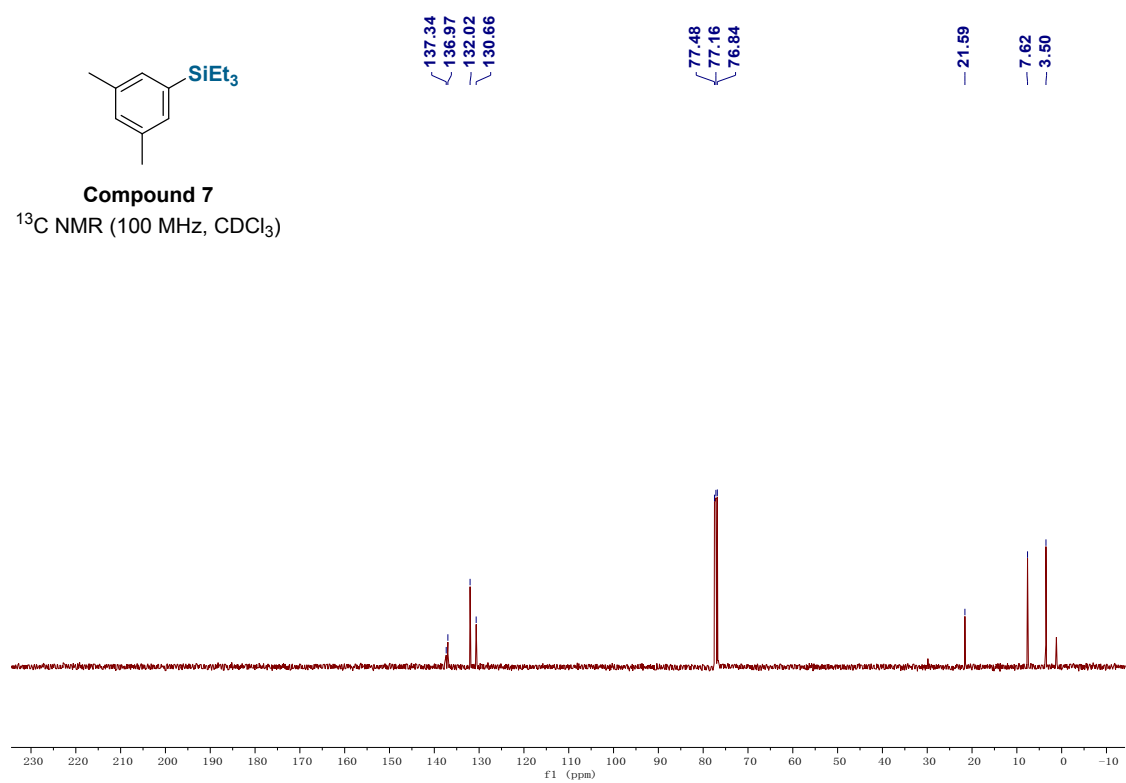
3,4-Dimethyl-1-(triethylsilyl)benzene (8)
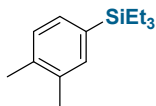
Compound 8

^{1}H NMR (400 MHz, CDCl$_3$)

7.260
7.243
7.227
7.140
7.122

2.274
2.264

0.983
0.964
0.944
0.801
0.782
0.762
0.743

2.01
0.99

6.00

9.25
6.24
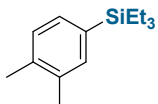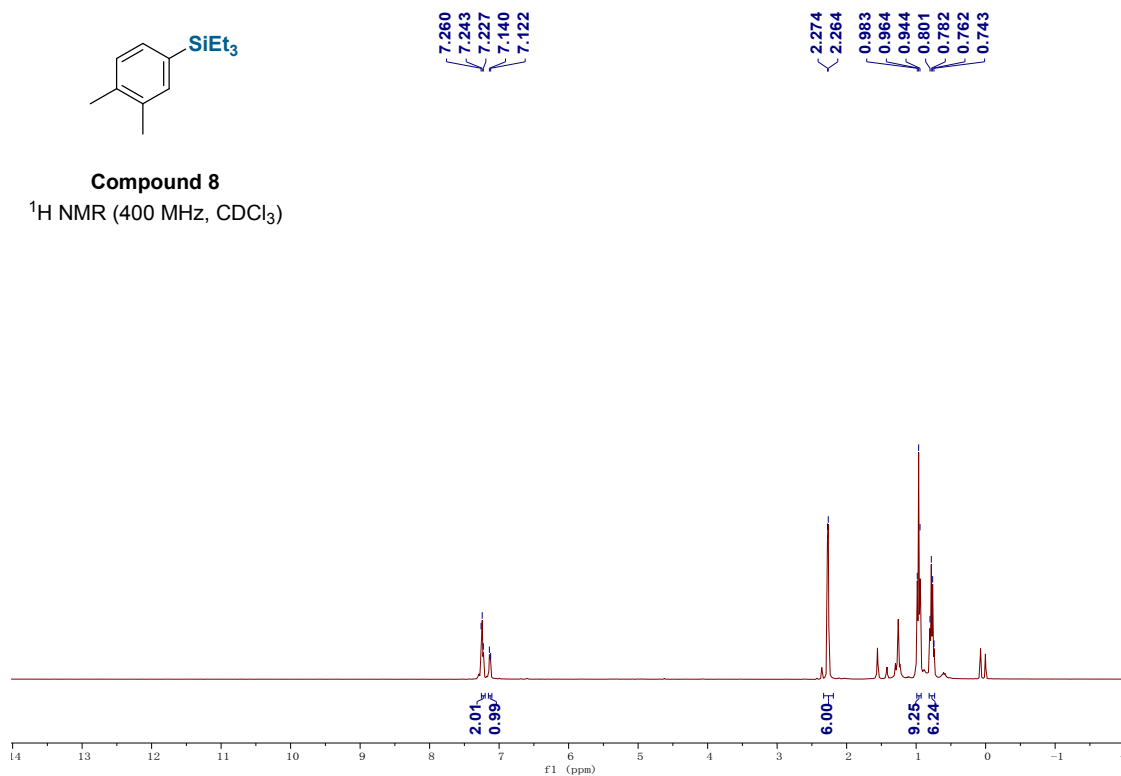
Compound 8

^{13}C NMR (100 MHz, CDCl$_3$)

137.39
135.91
135.62
134.44
132.01
129.22

77.48
77.16
76.84

29.86

19.94

7.61
3.54
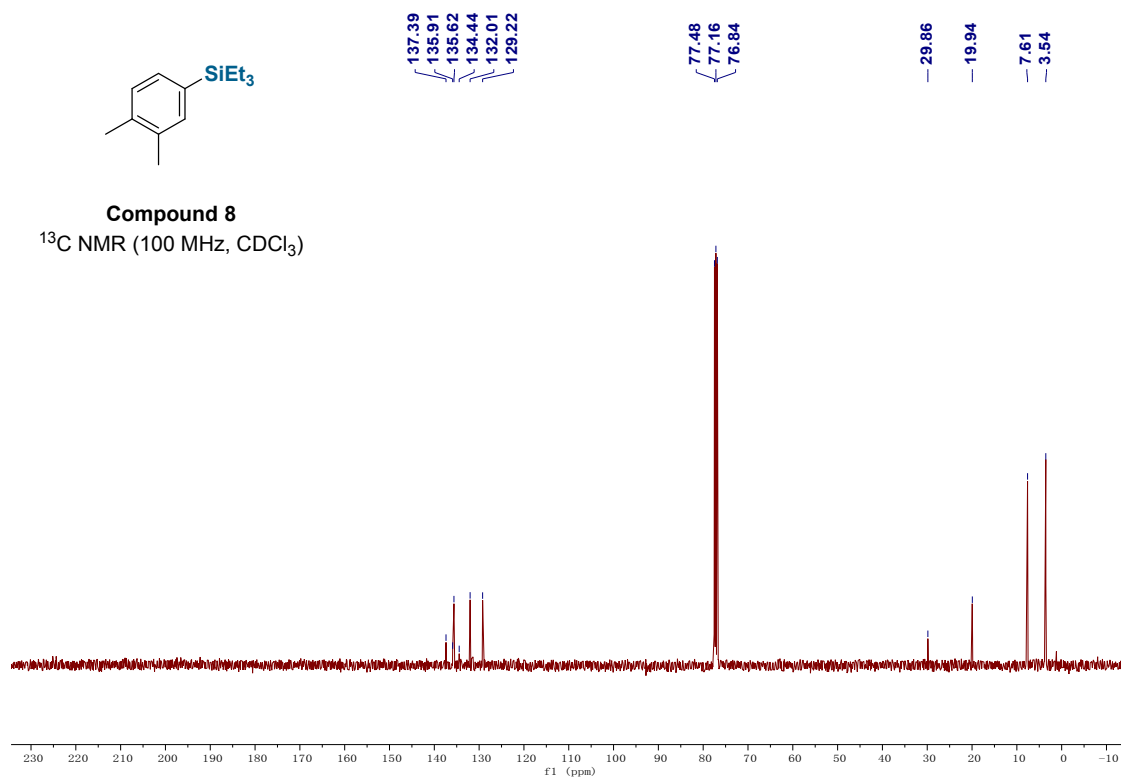
N, *N*-dimethyl-4-(triethylsilyl)aniline (9)

Compound 9

^{1}H NMR (400 MHz, CDCl$_3$)

7.393
7.372
6.764
6.743
2.972
0.994
0.974
0.955
0.792
0.774
0.754
0.733

1.97
2.02
6.07
9.00
6.07

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
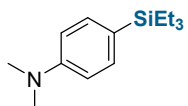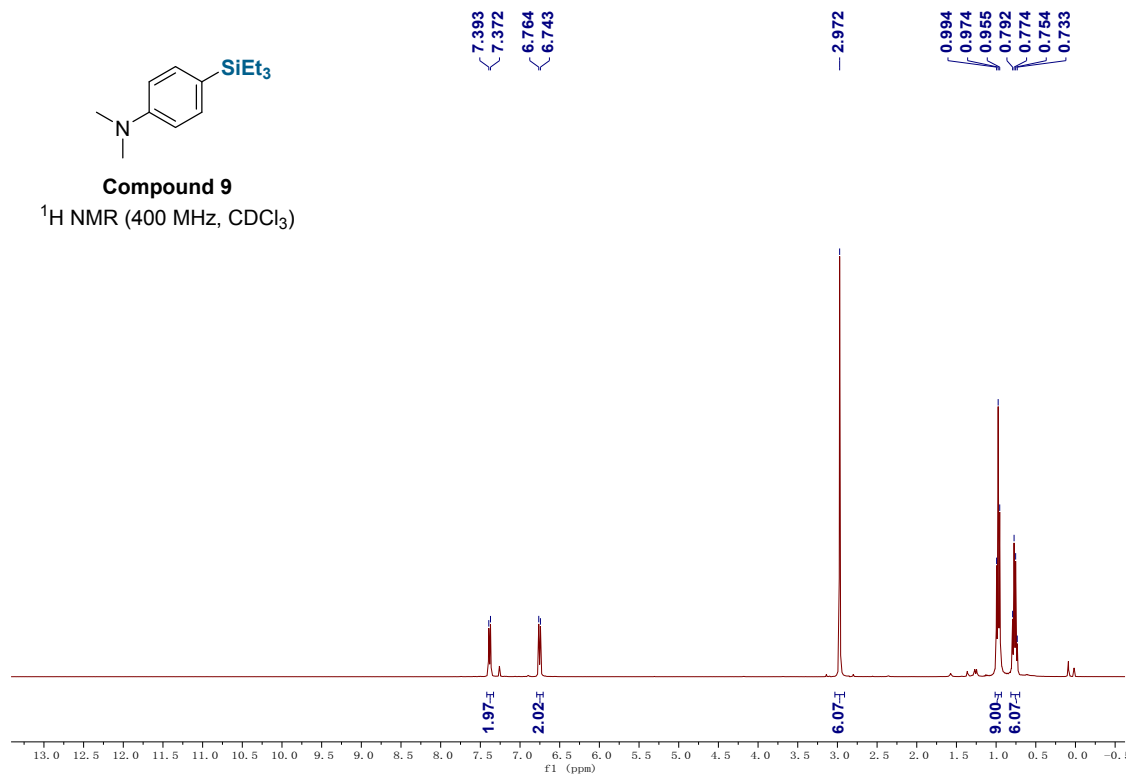
Compound 9

^{13}C NMR (100 MHz, CDCl$_3$)
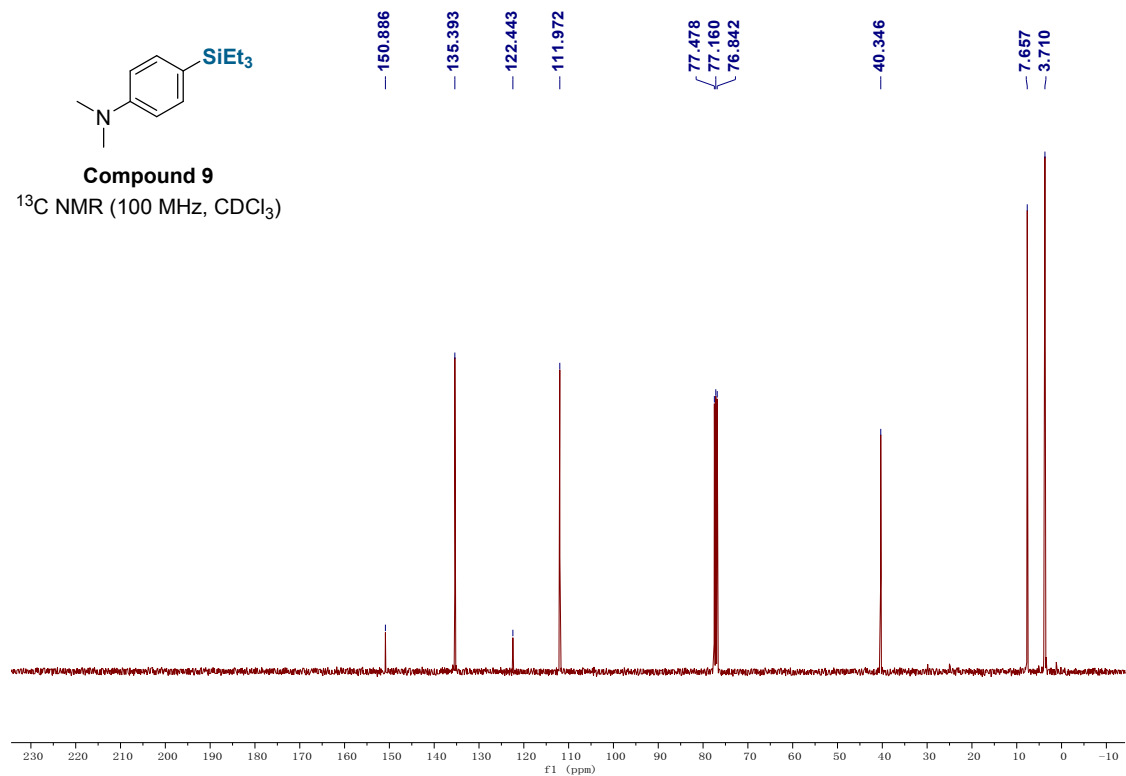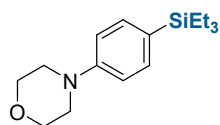
150.886
135.393
122.443
111.972
77.478
77.160
76.842
40.346
7.657
3.710

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

42

4-(4-(triethylsilyl)phenyl)morpholine (10).

Compound 10
^{1}H NMR (400 MHz, CDCl$_3$)
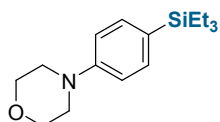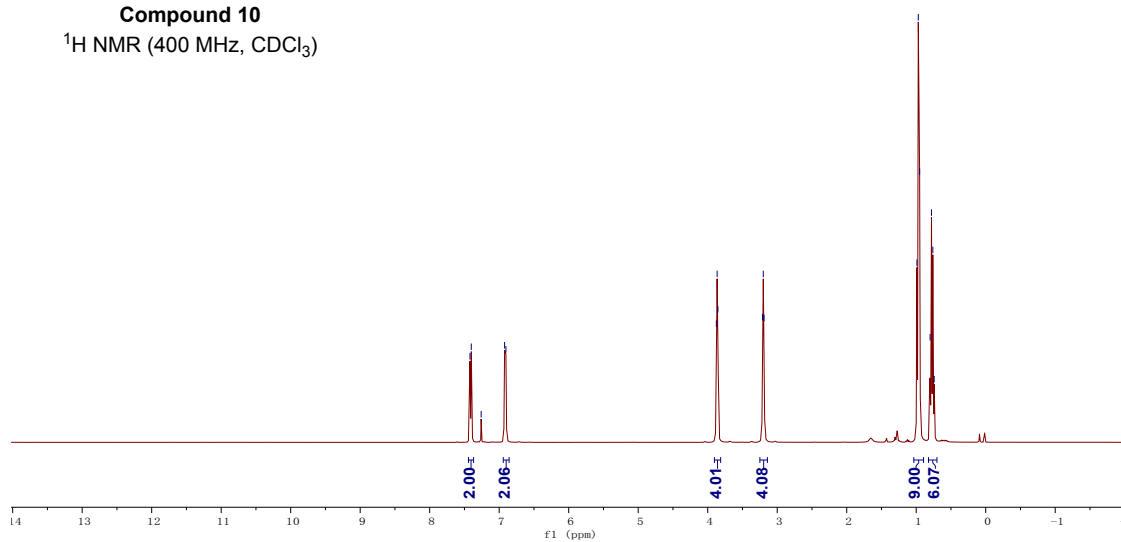
Compound 10
^{13}C NMR (100 MHz, CDCl$_3$)

N,N-dimethyl-1-(4-(triethylsilyl)phenyl)methanamine (11)

7.474
7.455
7.330
7.311
7.260

3.552

2.344

0.977
0.957
0.938
0.812
0.794
0.774
0.754
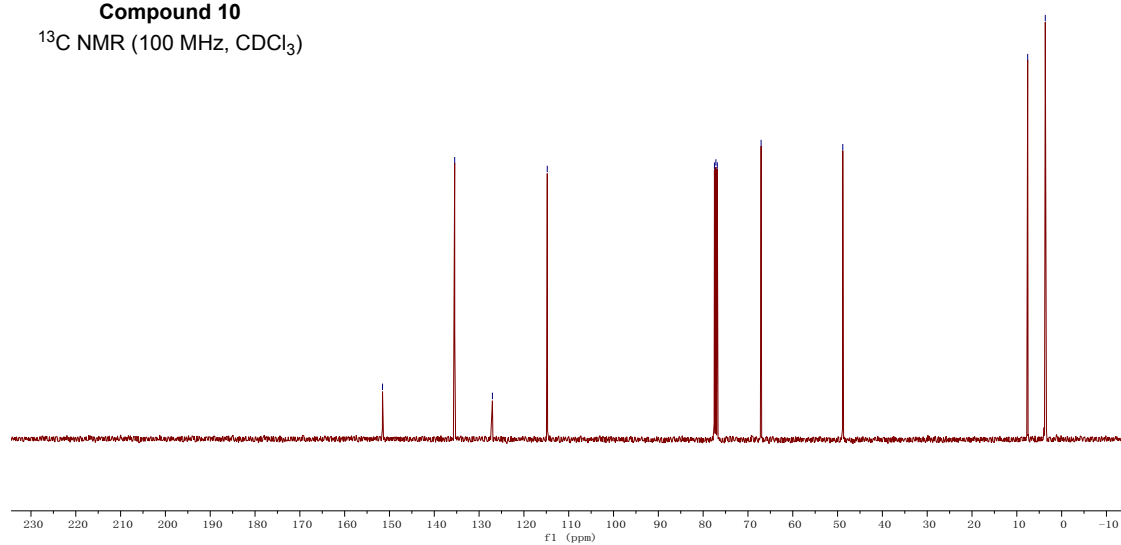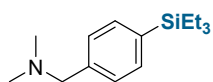
Compound 11
^{1}H NMR (400 MHz, CDCl$_3$)

2.00
2.03

2.02

6.03

9.04
6.26

f1 (ppm)

138.61
136.42
134.39
128.70

77.48
77.16
76.84

64.32

45.33

7.54
3.52
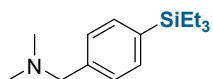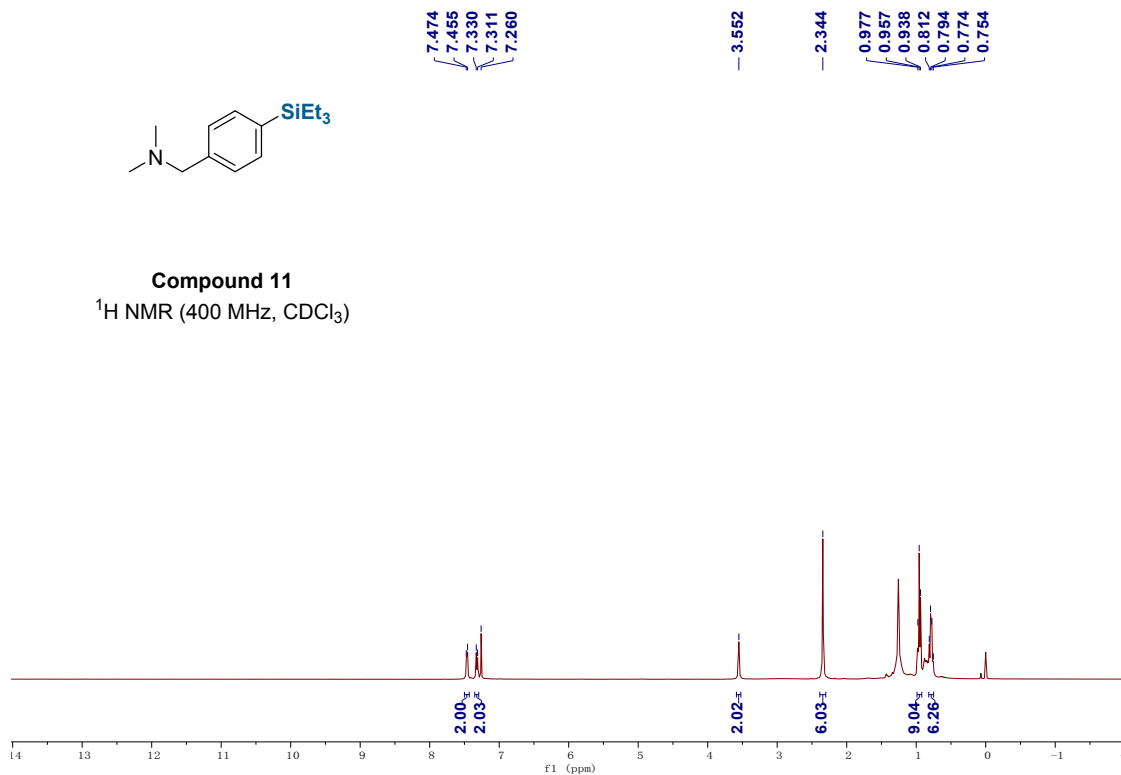
Compound 11
^{13}C NMR (100 MHz, CDCl$_3$)

f1 (ppm)

44
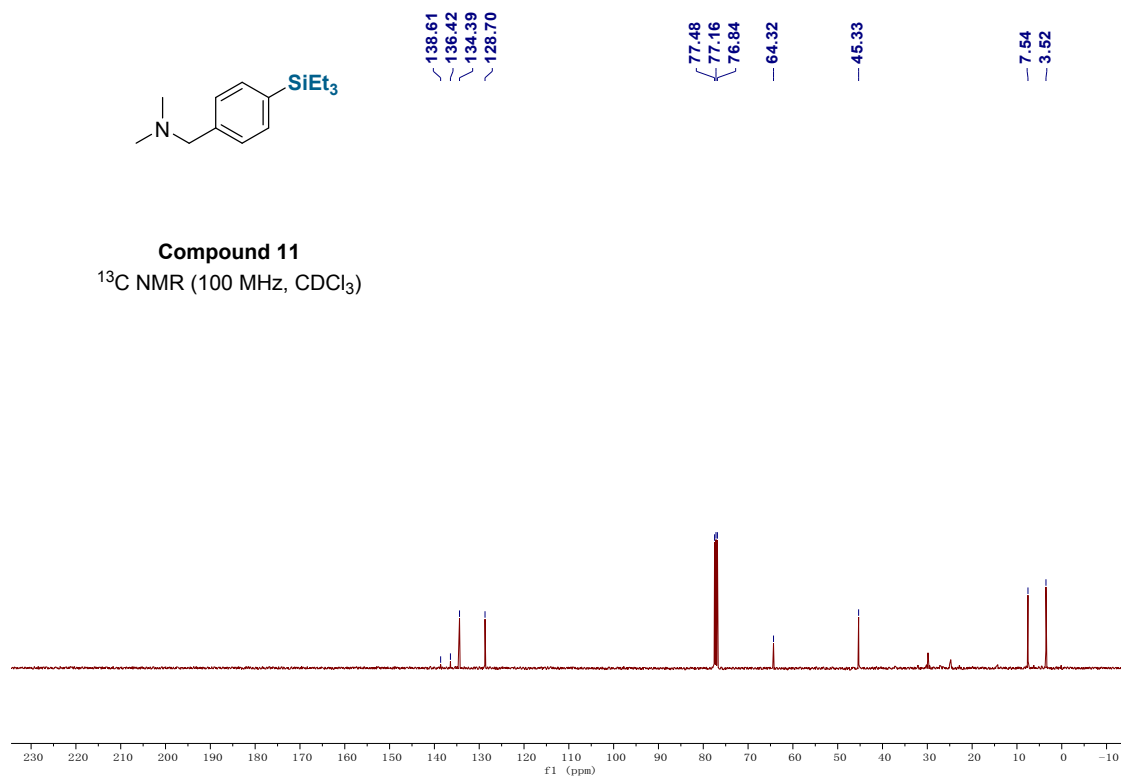
2-(4-(Triethylsilyl)phenyl)ethan-1-ol (12)
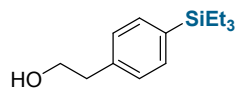
Compound 12

^{1}H NMR (400 MHz, CDCl$_3$)
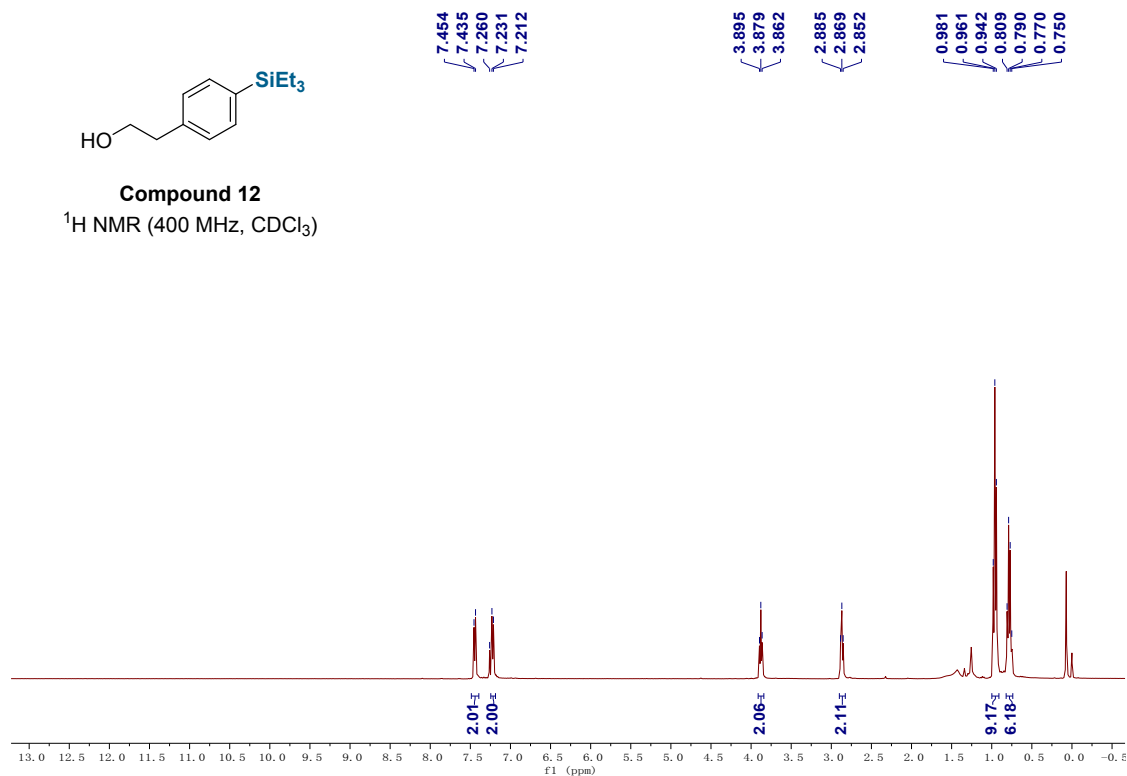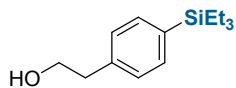
Compound 12
^{13}C NMR (100 MHz, CDCl$_3$)

139.01
135.40
134.67
128.57
77.48
77.16
76.84
63.74
39.33
7.56
3.49
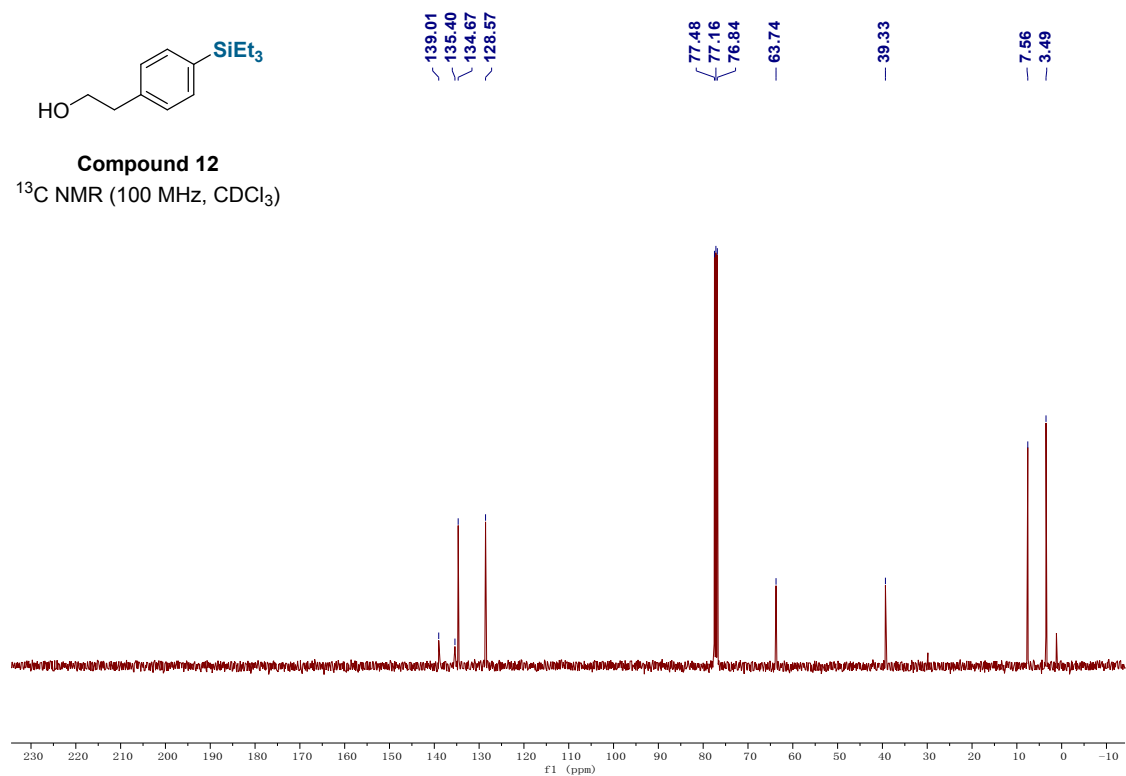
Triethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (13)
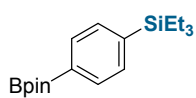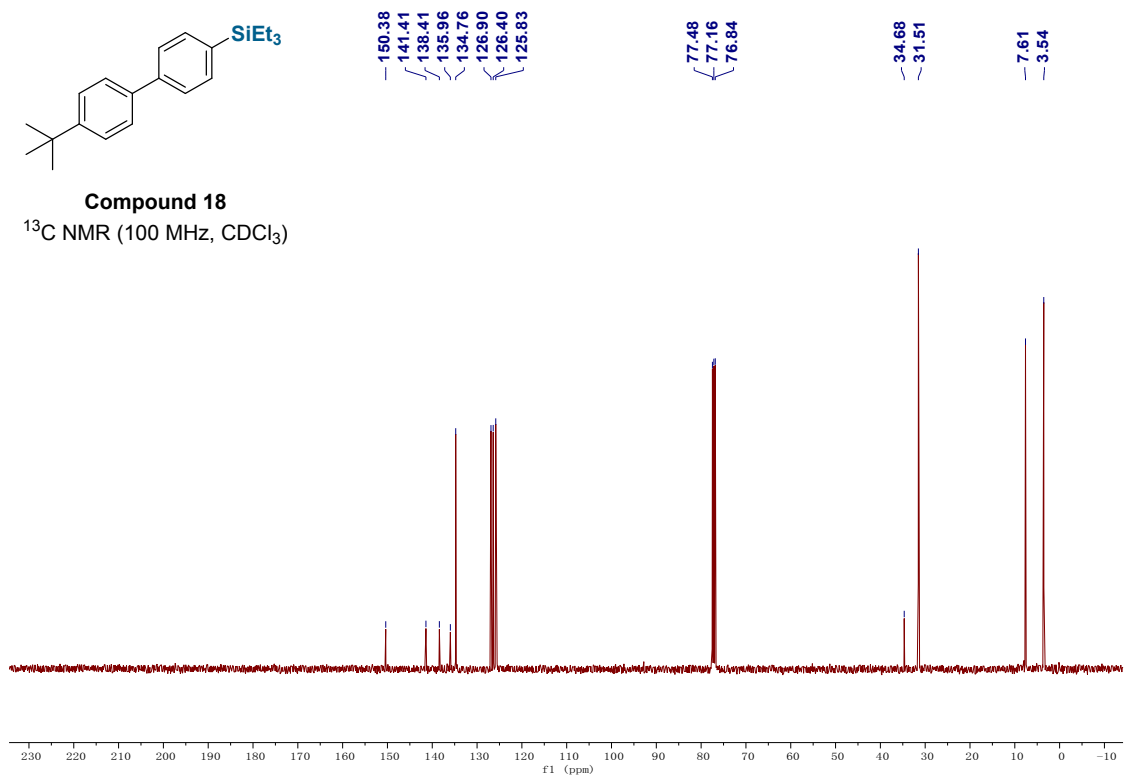

Compound 13
^{1}H NMR (400 MHz, CDCl$_3$)

7.791
7.772
7.514
7.495
7.260
1.340
0.969
0.950
0.931
0.819
0.801
0.781
0.762

2.00
2.00
12.11
9.07
6.05
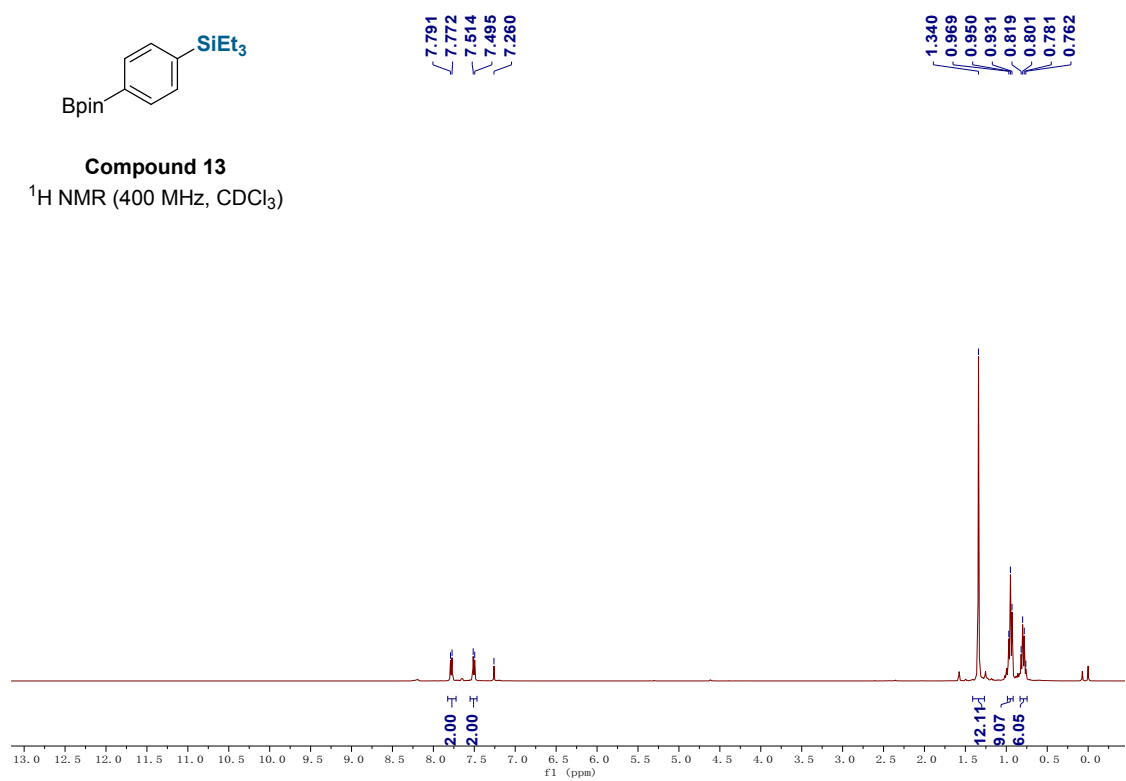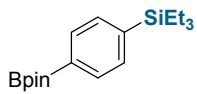
Compound 13

^{13}C NMR (100 MHz, CDCl$_3$)

141.44
133.86
133.68

83.86
77.48
77.16
76.84

24.99

7.51
3.34

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
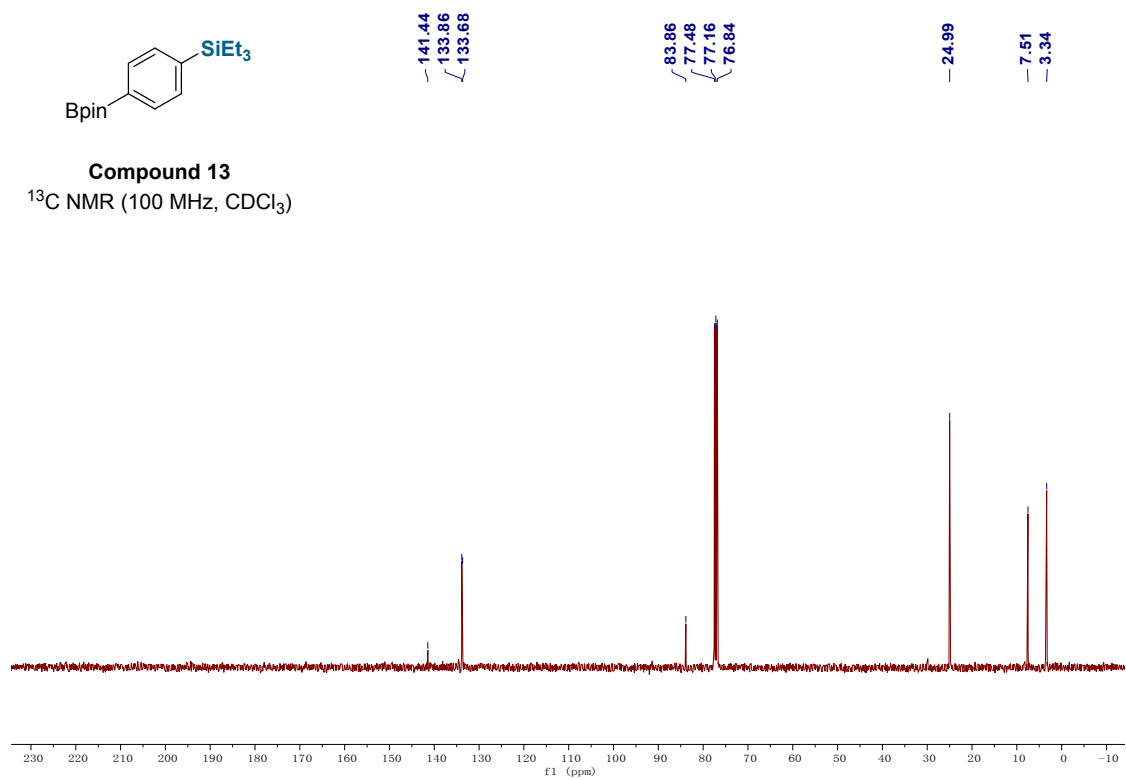
Triethyl(4-(trimethylsilyl)phenyl)silane (14)
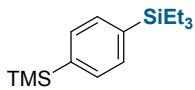
Compound 14

¹H NMR (400 MHz, CDCl₃)

7.525
7.521
7.506
7.496
7.490
7.480
7.476
7.260

1.002
0.982
0.963
0.830
0.811
0.792
0.772
0.276

3.97

9.23
6.00
8.96
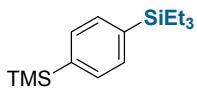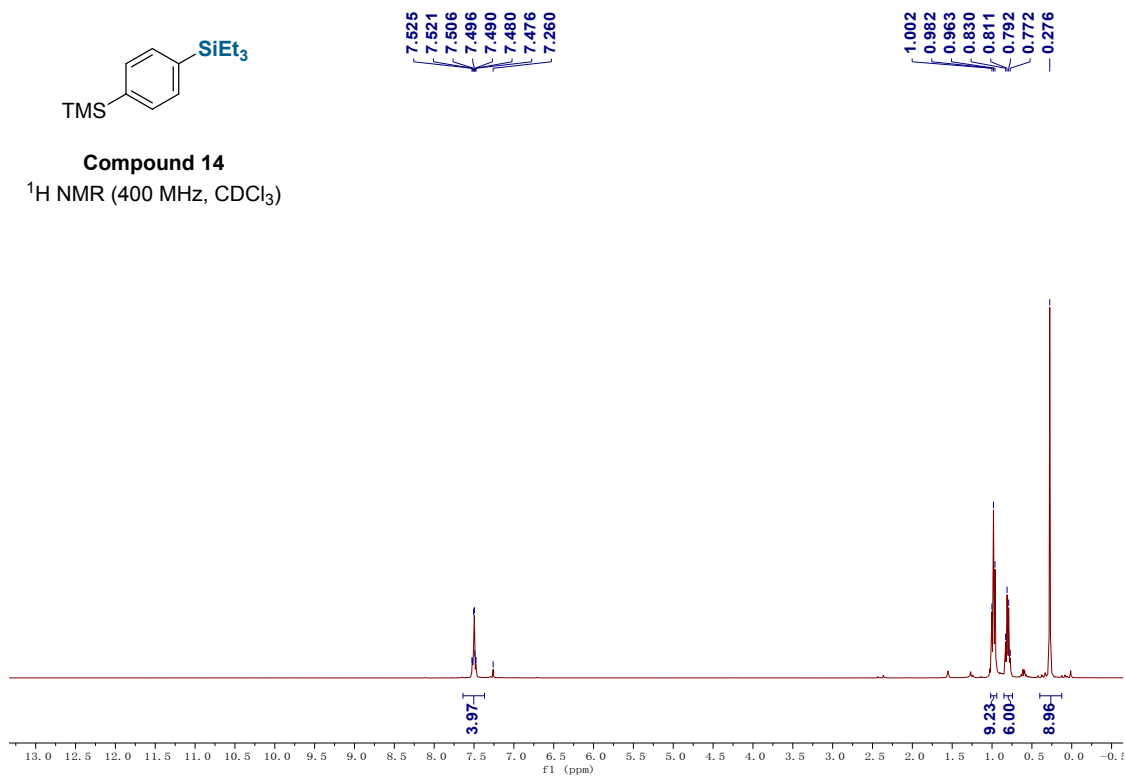
Compound 14

¹³C NMR (100 MHz, CDCl₃)

140.89
138.14
133.61
132.65

77.48
77.16
76.84

7.59
3.45
-1.03
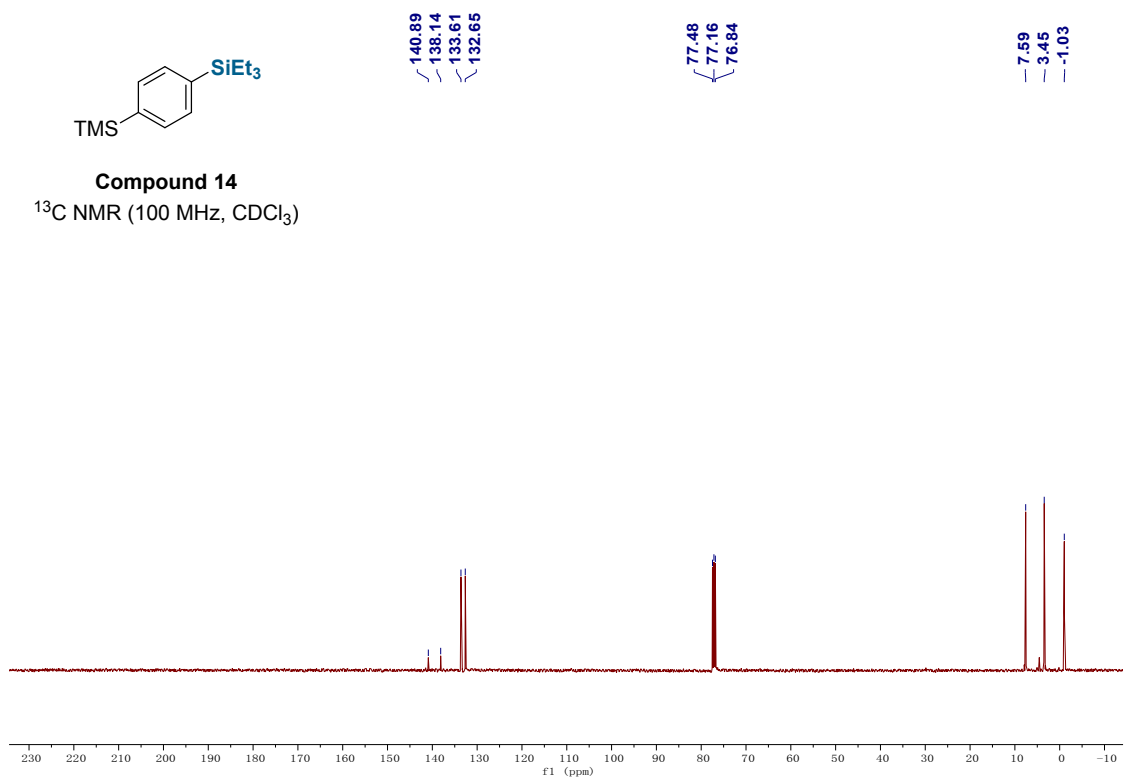
[1,1'-Biphenyl]-4-yltriethylsilane (15)
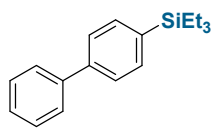
Compound 15
^{1}H NMR (400 MHz, CDCl$_3$)

7.647
7.628
7.606
7.604
7.484
7.465
7.446
7.386
7.368
7.350
7.260

1.043
1.023
1.004
0.881
0.862
0.843
0.823

6.02
2.11
1.00
9.03
6.10

13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
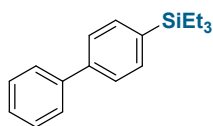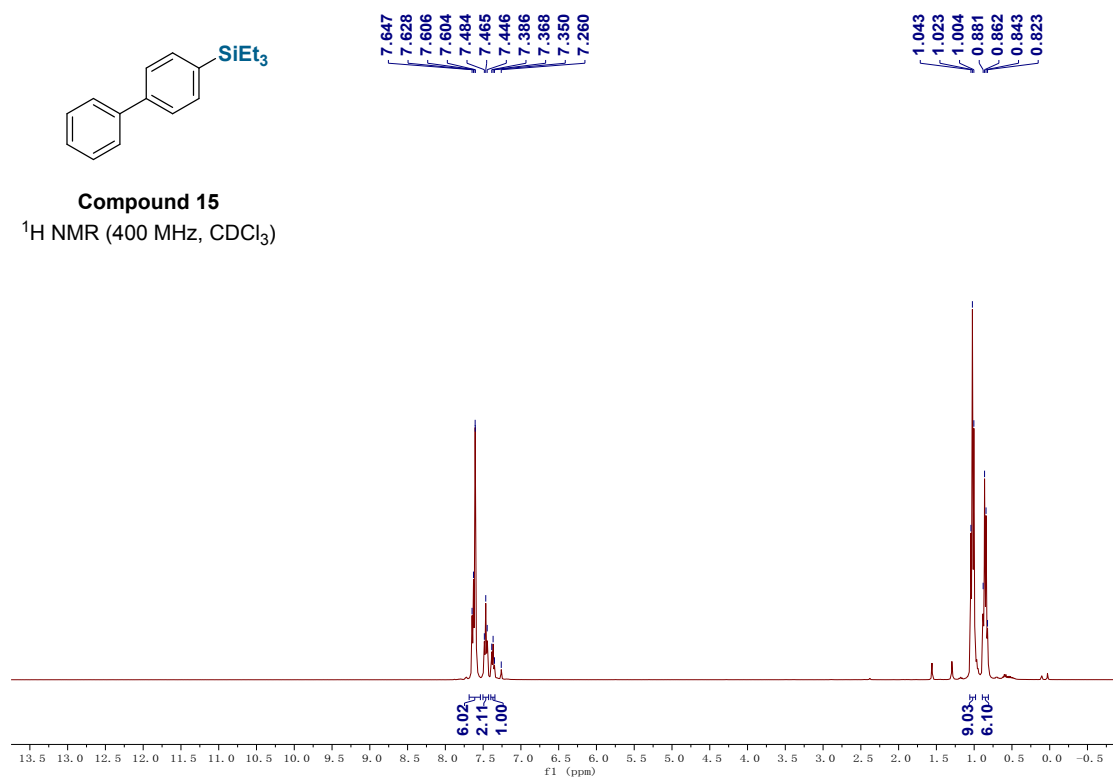
Compound 15
^{13}C NMR (100 MHz, CDCl$_3$)

141.52
141.28
136.34
134.82
128.87
127.41
127.27
126.52

77.48
77.16
76.84

7.60
3.50

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

49
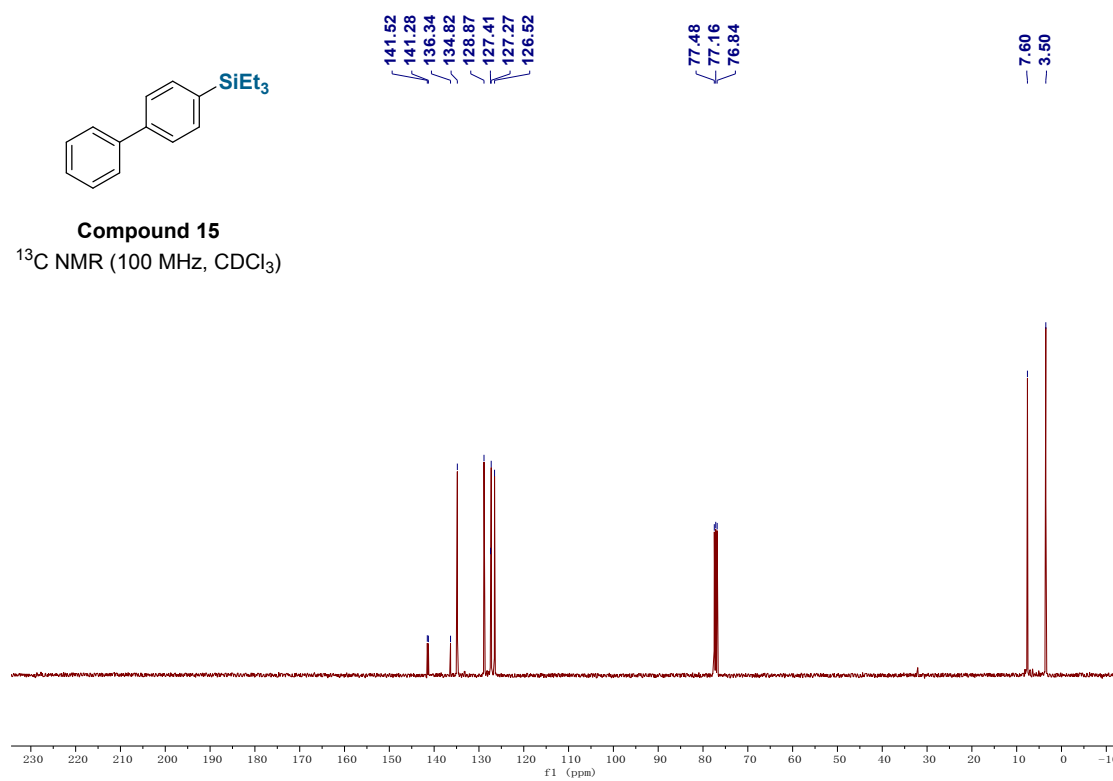
Triethyl(4'-methoxy-[1,1'-biphenyl]-4-yl)silane (16)
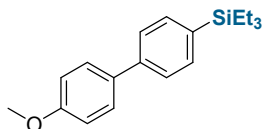
Compound 16

^{1}H NMR (400 MHz, CDCl$_3$)

7.573
7.568
7.559
7.552
7.260
7.002
6.981

3.862

1.027
1.007
0.989
0.862
0.843
0.823
0.804

6.12
2.17
3.19
9.00
6.06

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
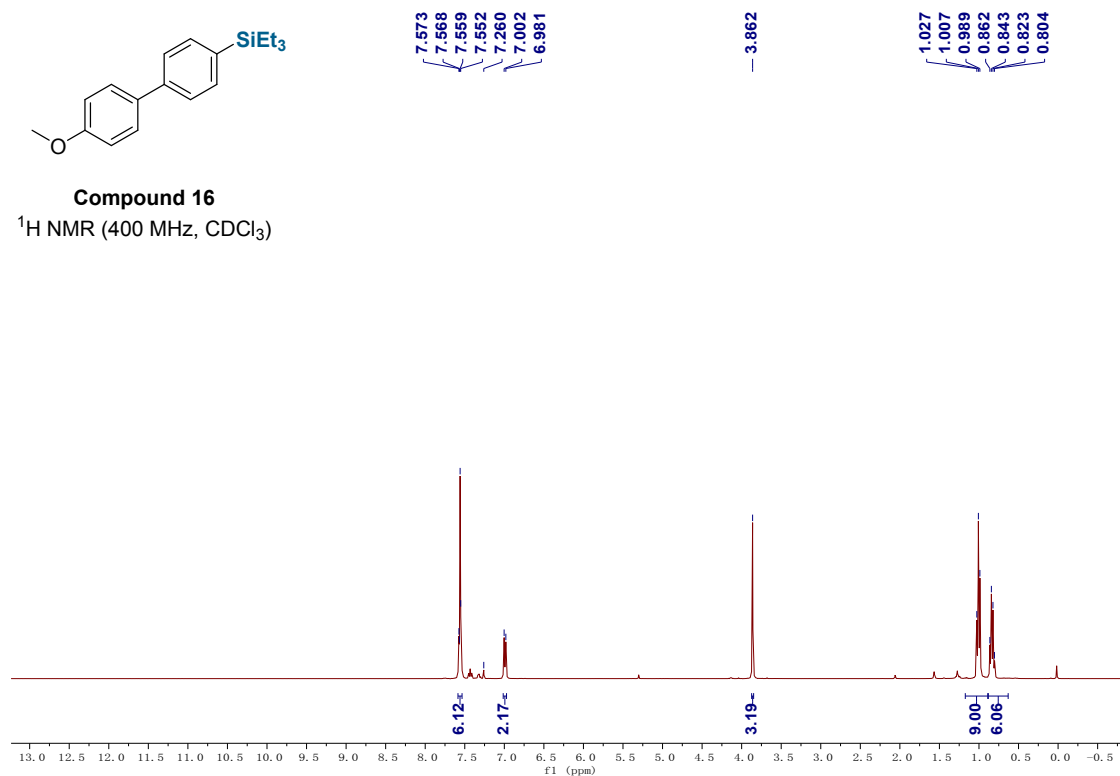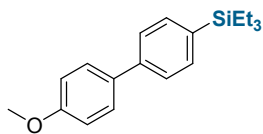
Compound 16

^{13}C NMR (100 MHz, CDCl$_3$)
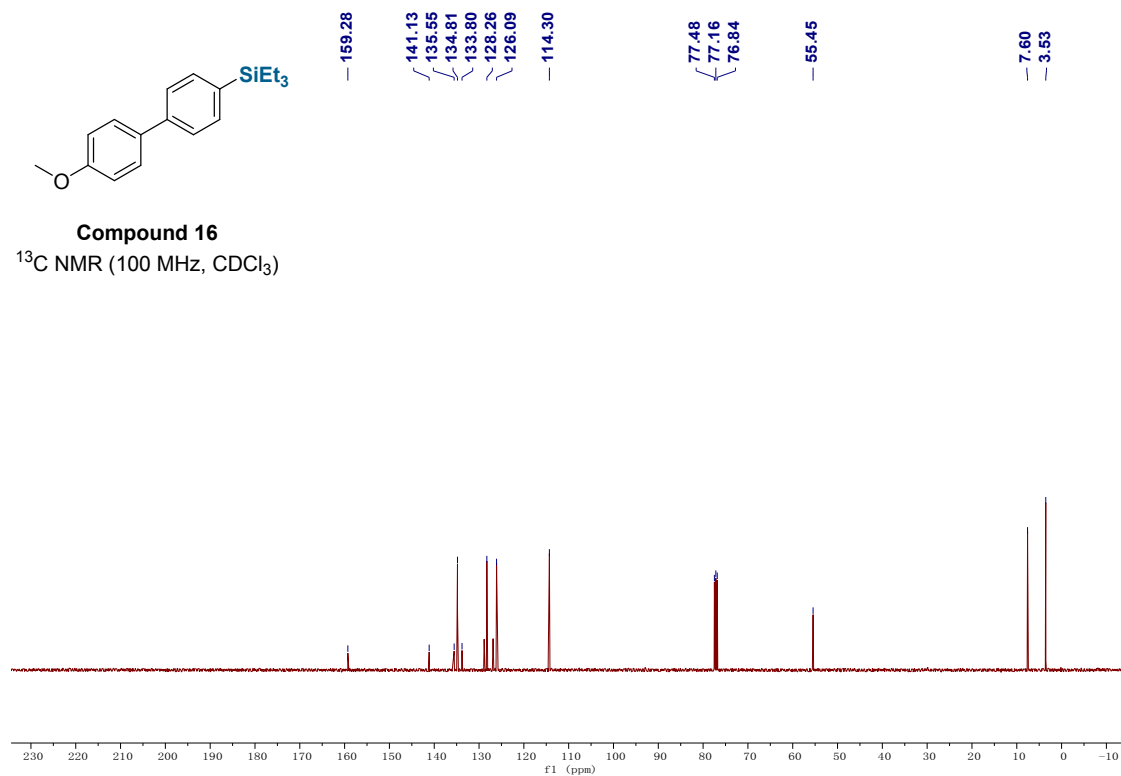
Triethyl(4'-phenoxy-[1,1'-biphenyl]-4-yl)silane (17)
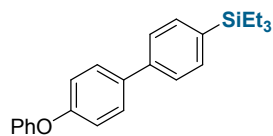
Compound 17

^{1}H NMR (400 MHz, CDCl$_3$)

Compound 17

^{13}C NMR (100 MHz, CDCl$_3$)

157.20, 156.98, 140.84, 136.29, 136.07, 134.85, 129.93, 128.52, 126.25, 123.52, 119.18, 119.11, 77.48, 77.16, 76.84, 7.60, 3.50
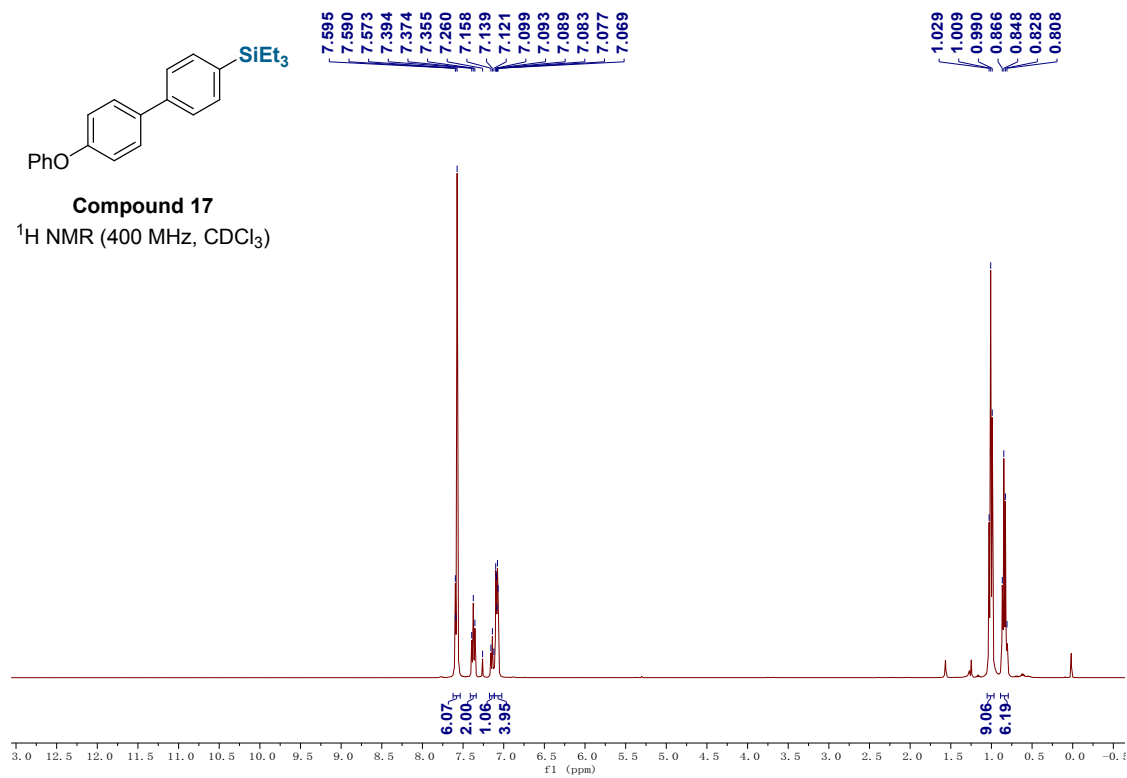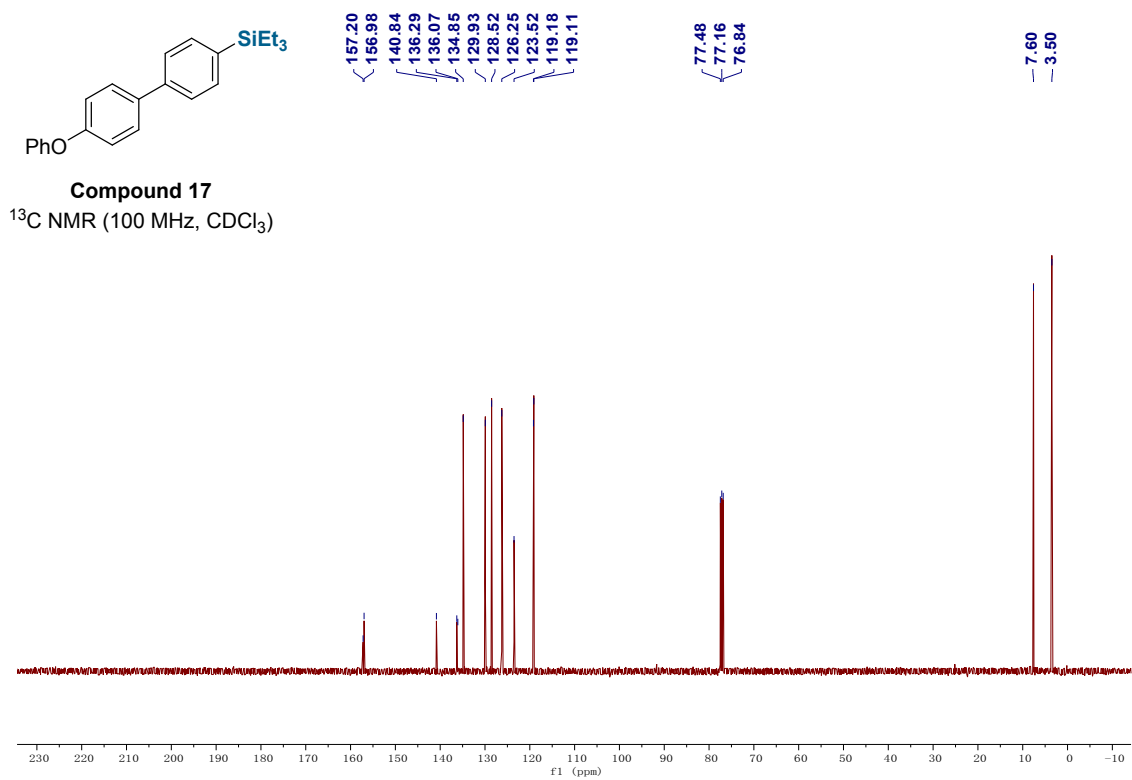
(4'-(Tert-butyl)-[1,1'-biphenyl]-4-yl)triethylsilane (18)
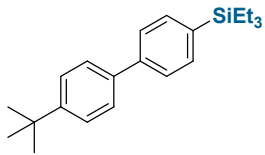
Compound 18

^{1}H NMR (400 MHz, CDCl$_3$)

7.600
7.580
7.573
7.557
7.553
7.488
7.468
7.260

1.377
1.029
1.009
0.990
0.864
0.845
0.825
0.806

6.01
2.02

9.14
9.06
6.00

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)
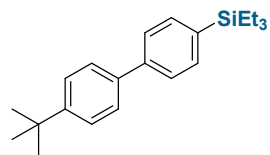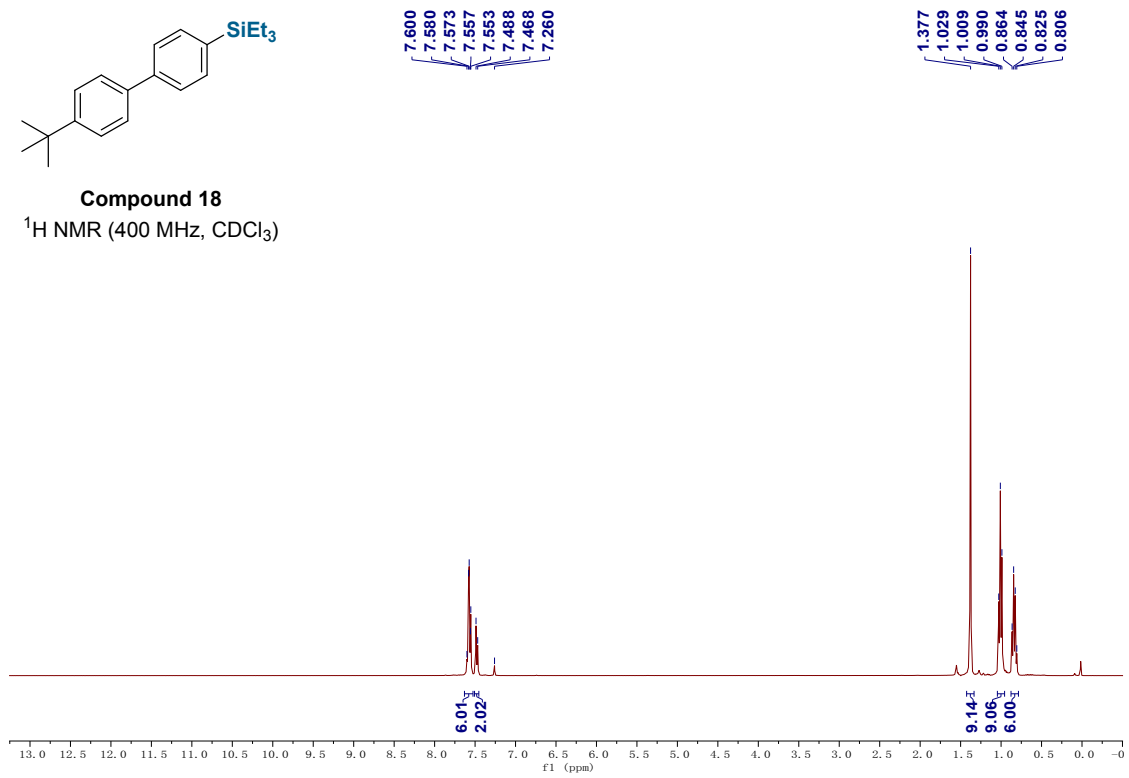
Compound 18

^{13}C NMR (100 MHz, CDCl$_3$)

150.38
141.41
138.41
135.96
134.76
126.90
126.40
125.83

77.48
77.16
76.84

34.68
31.51

7.61
3.54

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

Triethyl(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)silane (19)

Compound 19

^{1}H NMR (400 MHz, CDCl$_3$)
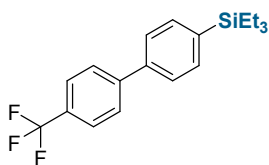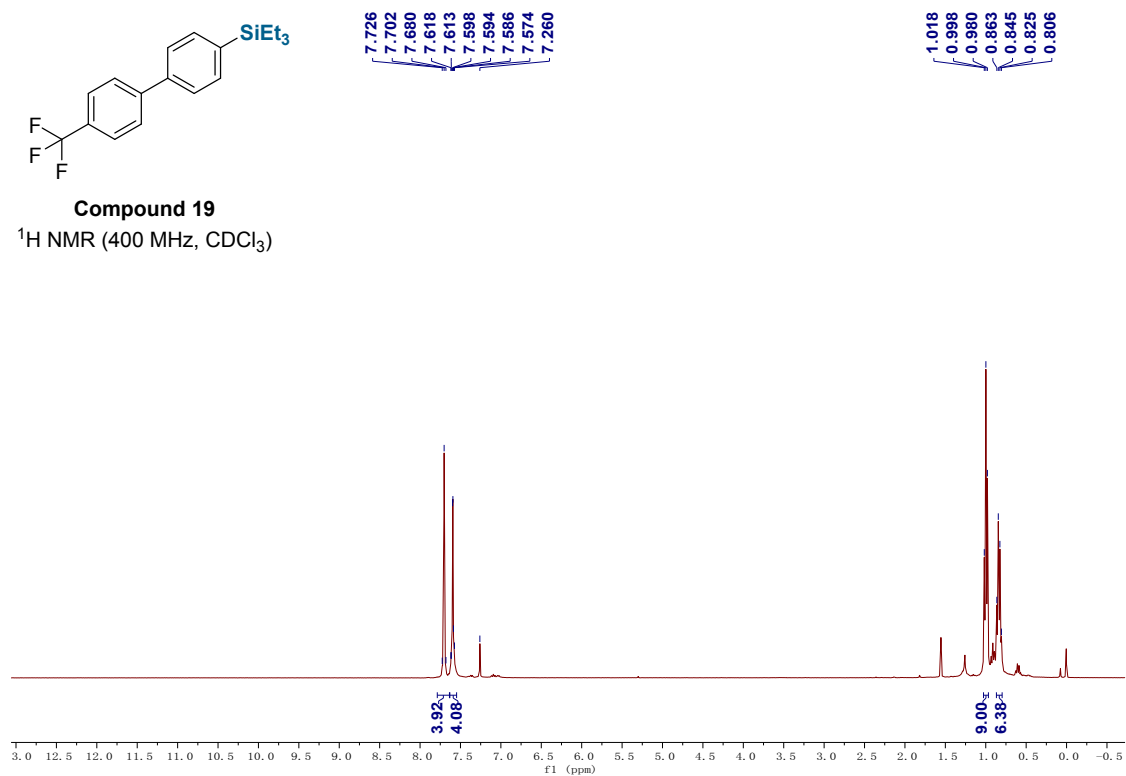
Compound 19

^{13}C NMR (100 MHz, CDCl$_3$)
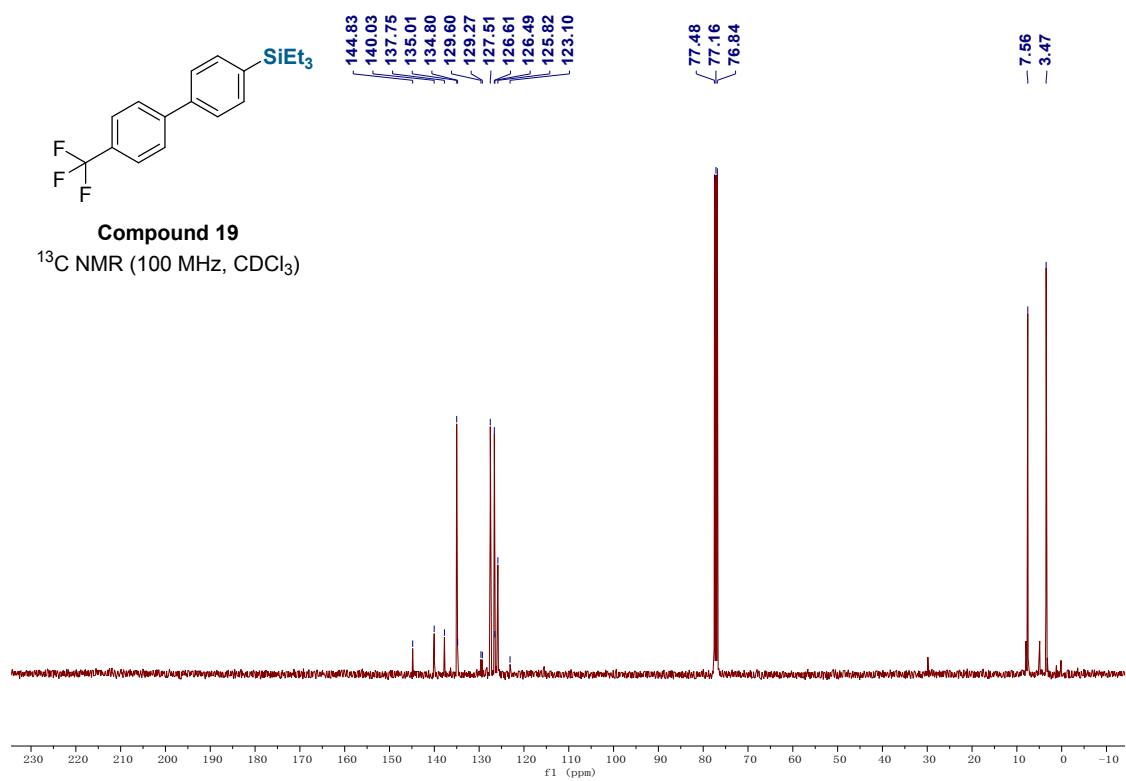
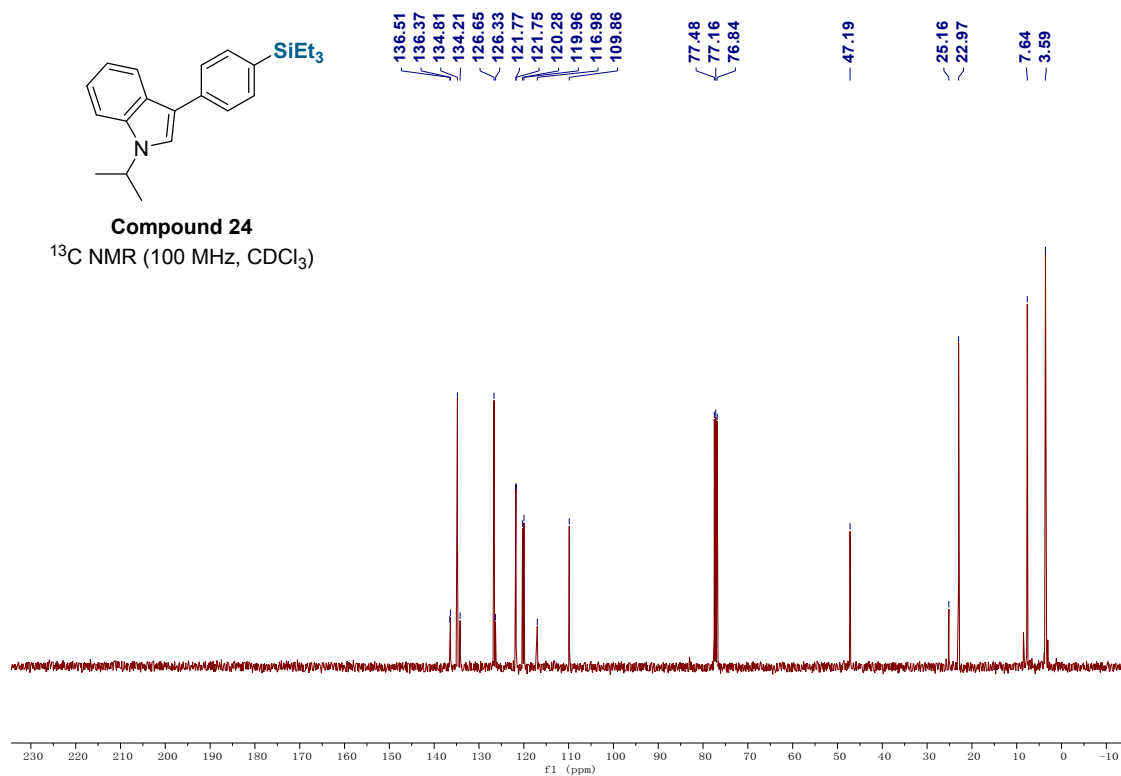# [1,1':4',1''-Terphenyl]-4-yltriethylsilane (20)
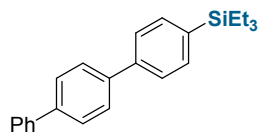
Compound 20

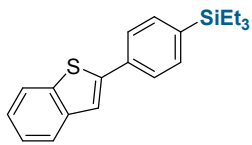^{1}H NMR (400 MHz, CDCl$_3$)

Compound 20
^{13}C NMR (100 MHz, CDCl$_3$)

4-(4'-(Triethylsilyl)-[1,1'-biphenyl]-4-yl)morpholine (21)

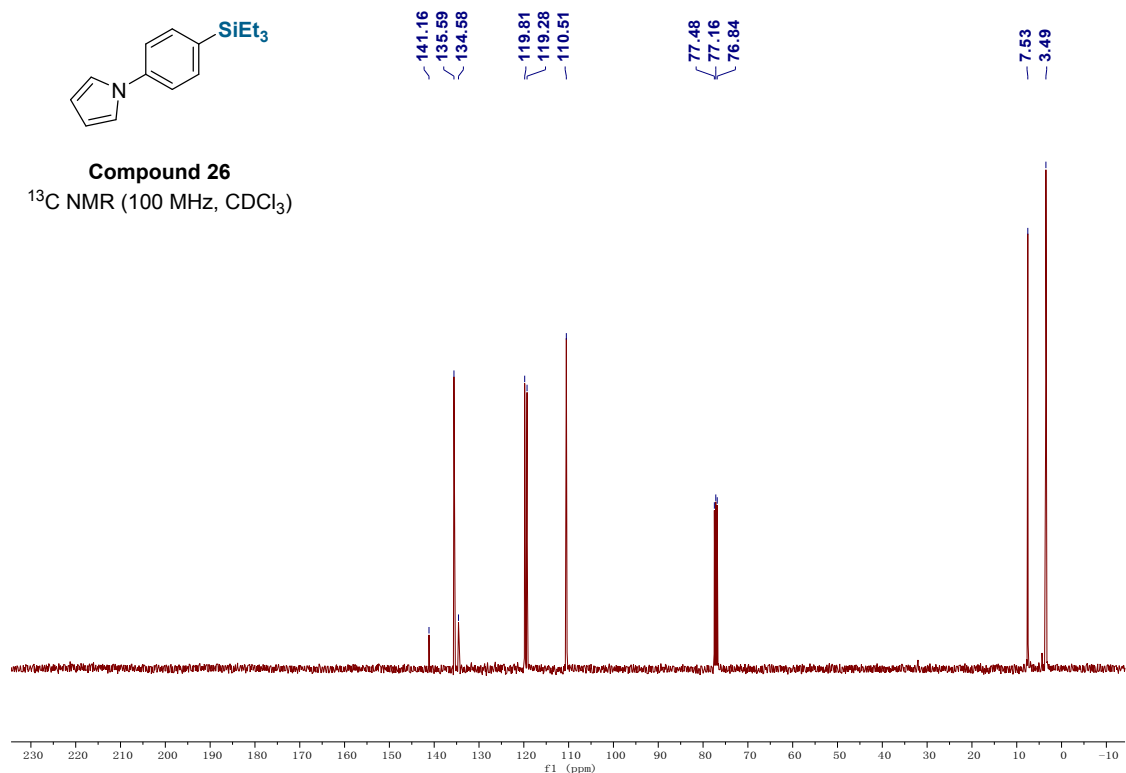Compound 21
^{1}H NMR (400 MHz, CDCl$_3$)

Compound 21
^{13}C NMR (100 MHz, CDCl$_3$)

150.64
141.11
135.35
134.79
132.69
127.90
125.88
115.82
77.48
77.16
76.84
67.03
49.23
7.60
3.52

Triethyl(4-(naphthalen-1-yl)phenyl)silane (22)

Compound 22

^{1}H NMR (400 MHz, CDCl$_3$)

7.992
7.971
7.941
7.921
7.892
7.871
7.649
7.630
7.569
7.551
7.530
7.504
7.474
7.457
7.440
7.260

1.086
1.066
1.047
0.923
0.904
0.884
0.865

1.01
1.01
1.01
2.00
6.18

9.03
6.10

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)

Compound 22

^{13}C NMR (100 MHz, CDCl$_3$)

141.10
140.43
136.33
134.25
133.92
131.67
130.21
129.46
128.39
127.71
127.07
126.25
126.15
126.11
125.89
125.54

77.48
77.16
76.84

7.66
3.57

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

58

Triethyl(4-(naphthalen-2-yl)phenyl)silane (23)

8.083 7.946 7.926 7.910 7.895 7.889 7.878 7.872 7.800 7.775 7.750 7.730 7.647 7.627 7.547 7.542 7.530 7.525 7.518 7.512 7.506 7.499 7.495 7.482 7.477 7.260

1.054 1.034 1.015 0.894 0.877 0.857 0.838

Compound 23
^{1}H NMR (400 MHz, CDCl$_3$)

1.03 3.08 1.02 2.03 2.00 2.03

9.05 6.02

141.40 138.61 136.50 134.92 133.78 132.76 128.53 128.35 127.77 126.77 126.38 126.05 125.92 125.69

77.48 77.16 76.84

7.61 3.51

Compound 23
^{13}C NMR (100 MHz, CDCl$_3$)

1-Isopropyl-3-(4-(triethylsilyl)phenyl)-1H-indole (24)

Compound 24
^{1}H NMR (400 MHz, CDCl$_3$)
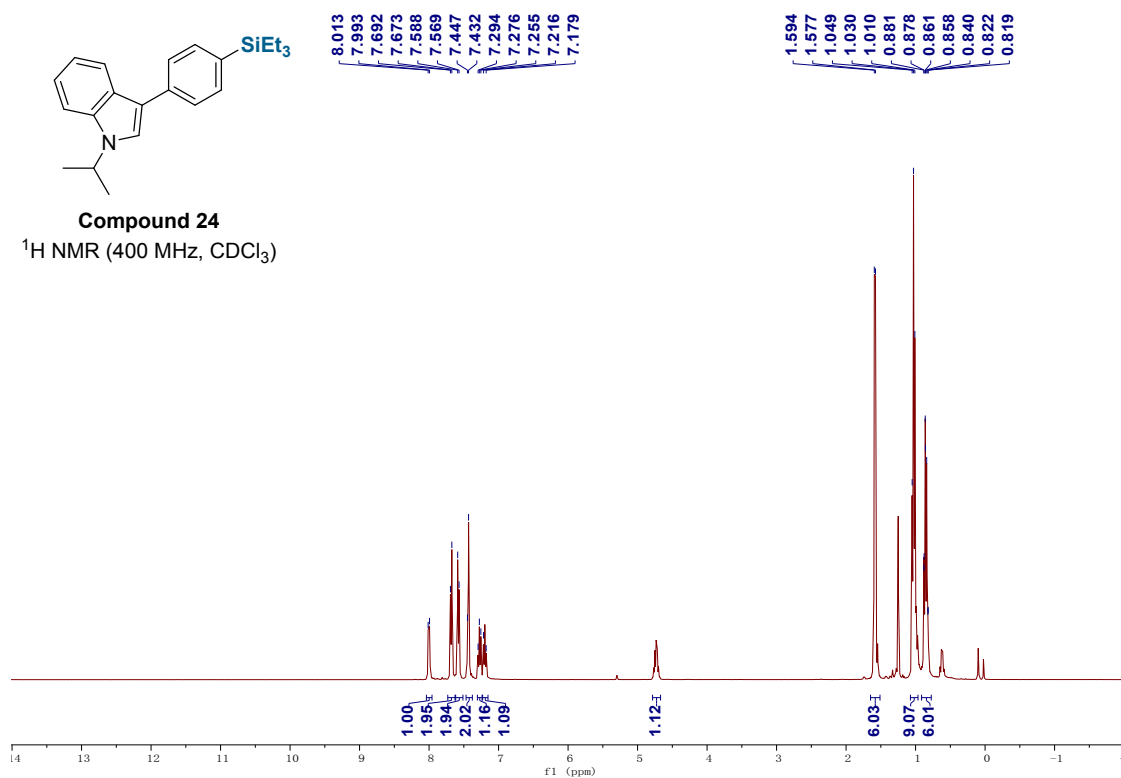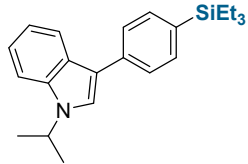
Compound 24

^{13}C NMR (100 MHz, CDCl$_3$)

Peaks: 136.51, 136.37, 134.81, 134.21, 126.65, 126.33, 121.77, 121.75, 120.28, 119.96, 116.98, 109.86, 77.48, 77.16, 76.84, 47.19, 25.16, 22.97, 7.64, 3.59

(4-(Benzo[b]thiophen-2-yl)phenyl)triethylsilane (25)
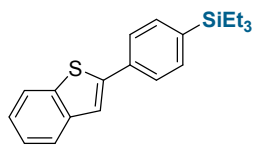
Compound 25

^1H NMR (400 MHz, CDCl$_3$)

Peaks: 7.856, 7.836, 7.802, 7.783, 7.730, 7.711, 7.593, 7.581, 7.562, 7.387, 7.370, 7.347, 7.325, 7.307, 7.260, 1.032, 1.012, 0.993, 0.872, 0.853, 0.833, 0.813

Integrations: 0.95, 0.96, 1.99, 2.01, 1.00, 2.14, 9.22, 6.29
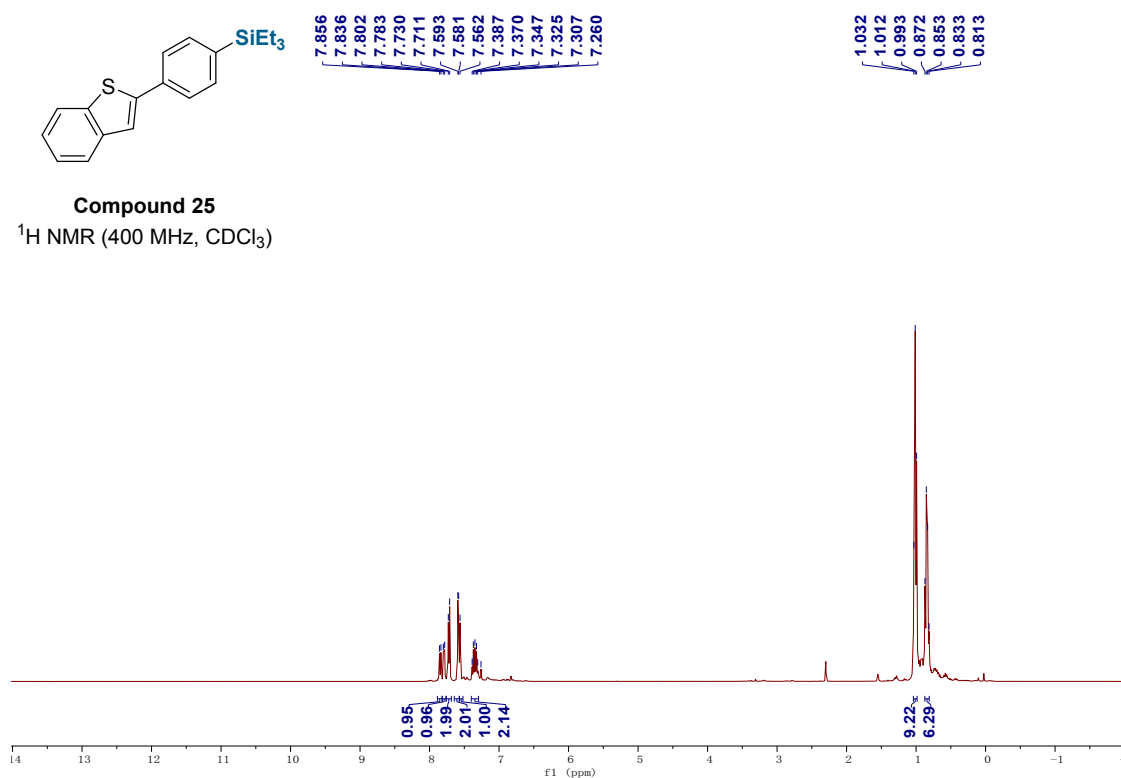
Compound 25

^{13}C NMR (100 MHz, CDCl$_3$)

144.51
140.82
139.61
138.02
134.94
134.58
125.74
124.61
124.44
123.70
122.42
119.54

77.48
77.16
76.84

7.56
3.44

1-(4-(Triethylsilyl)phenyl)-1H-pyrrole (26)

7.568
7.547
7.412
7.392
7.260
7.136

6.370

1.023
1.003
0.984
0.860
0.841
0.821
0.803
0.799
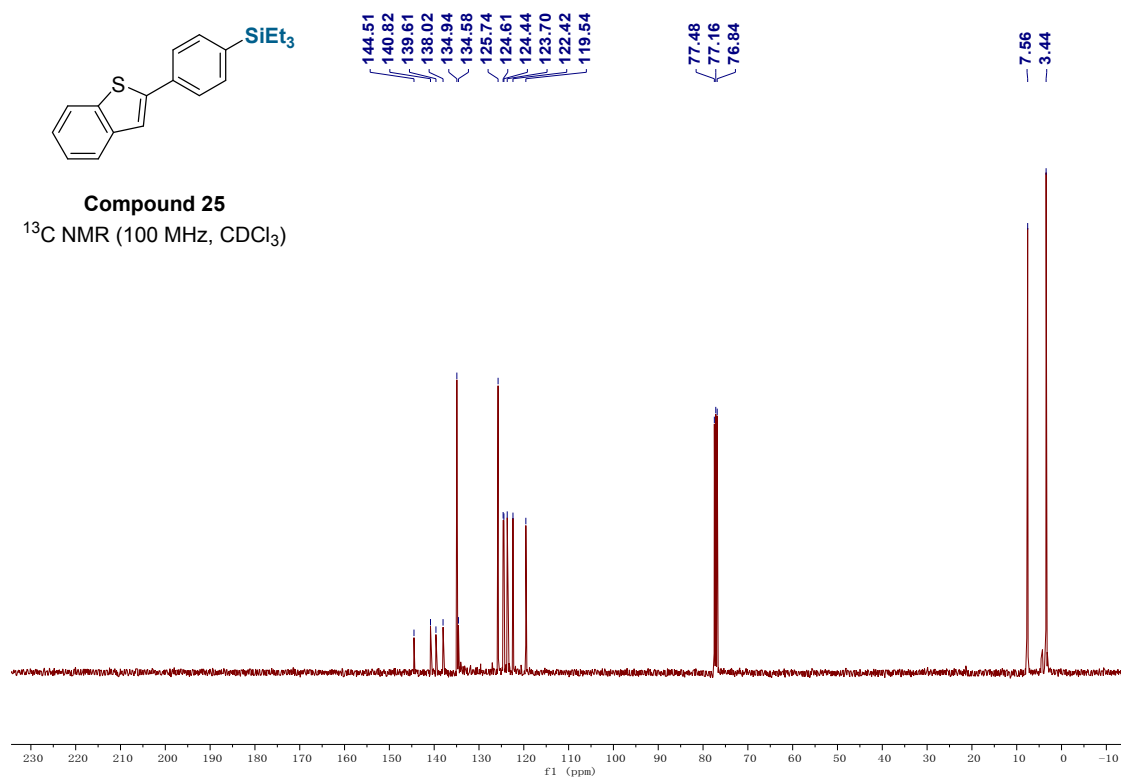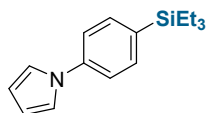
Compound 26

^{1}H NMR (400 MHz, CDCl$_3$)

2.01
2.00
2.02

2.03

9.00
6.08
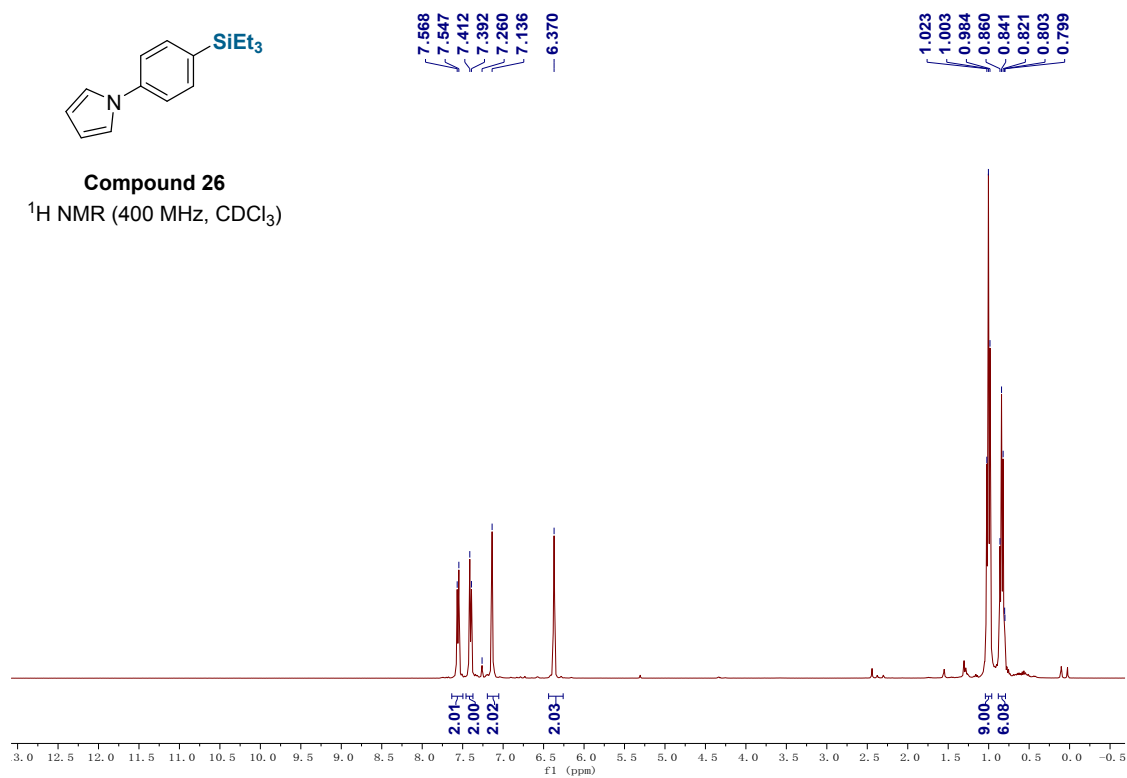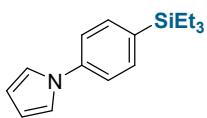
Compound 26
^{13}C NMR (100 MHz, CDCl$_3$)

141.16
135.59
134.58
119.81
119.28
110.51
77.48
77.16
76.84
7.53
3.49

Triethyl(naphthalen-2-yl)silane (27)

Compound 27
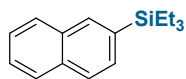
^{1}H NMR (400 MHz, CDCl$_3$)

8.002
7.872
7.864
7.858
7.850
7.844
7.835
7.824
7.601
7.581
7.504
7.496
7.488
7.480
7.260

1.039
1.020
1.001
0.926
0.909
0.890
0.868

1.00
3.00
1.06
2.07

3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

Compound 27

^{13}C NMR (100 MHz, CDCl$_3$)
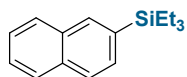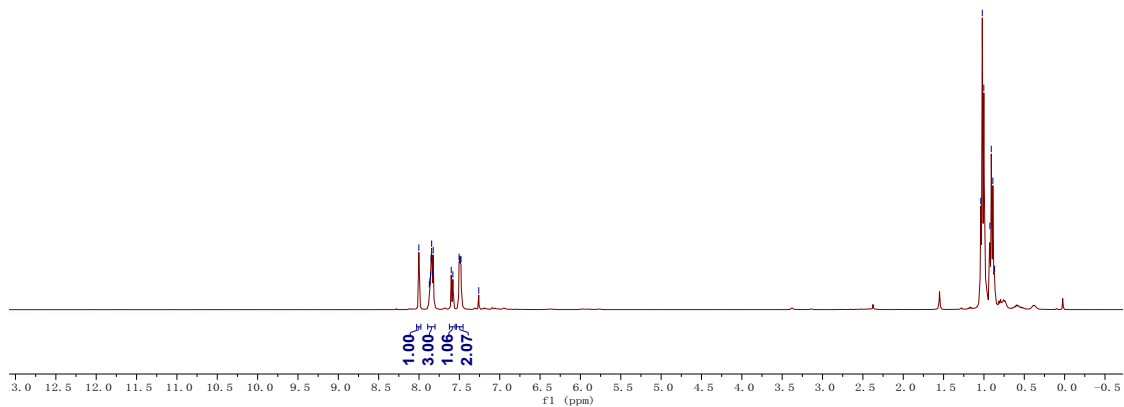
135.12
134.94
133.75
133.08
130.74
128.14
127.82
126.88
126.27
125.88

77.48
77.16
76.84

7.61
3.53

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

64
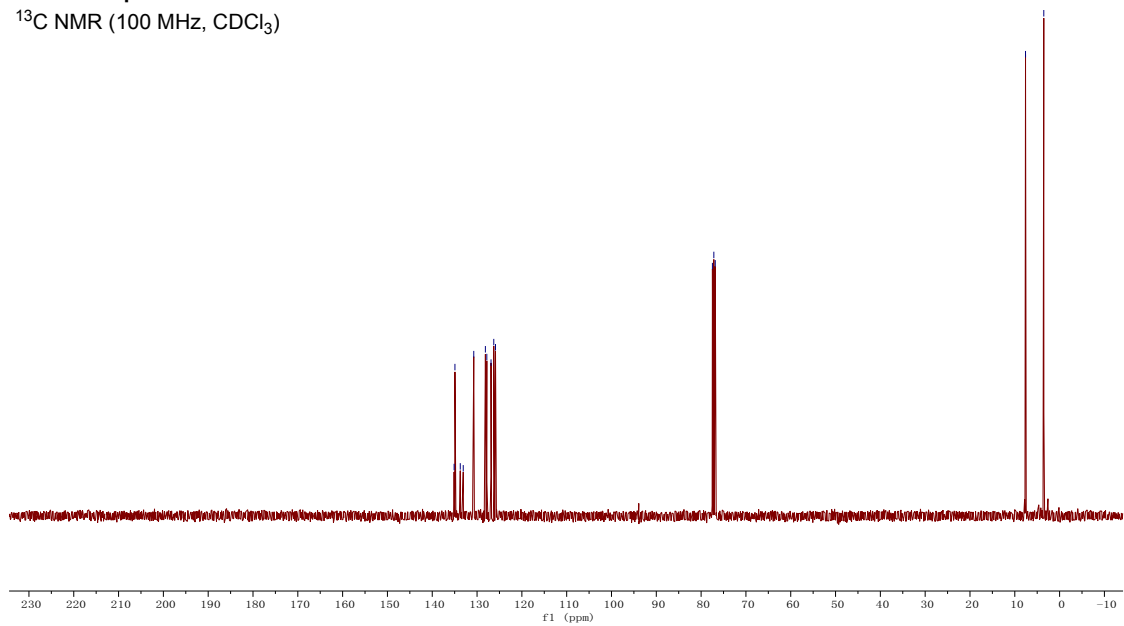
Triethyl(naphthalen-1-yl)silane (28)
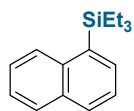
Compound 28

^{1}H NMR (400 MHz, CDCl$_3$)

8.128, 8.121, 8.112, 8.104, 7.886, 7.881, 7.877, 7.869, 7.862, 7.856, 7.698, 7.681, 7.530, 7.525, 7.513, 7.506, 7.497, 7.487, 7.483, 7.466, 7.463, 7.446, 7.260

1.064, 1.050, 1.045, 1.029, 1.018, 1.014, 1.003, 1.000, 0.988, 0.980, 0.973, 0.967, 0.957

1.01, 2.00, 1.03, 2.97, 15.00

f1 (ppm)

SiEt₃
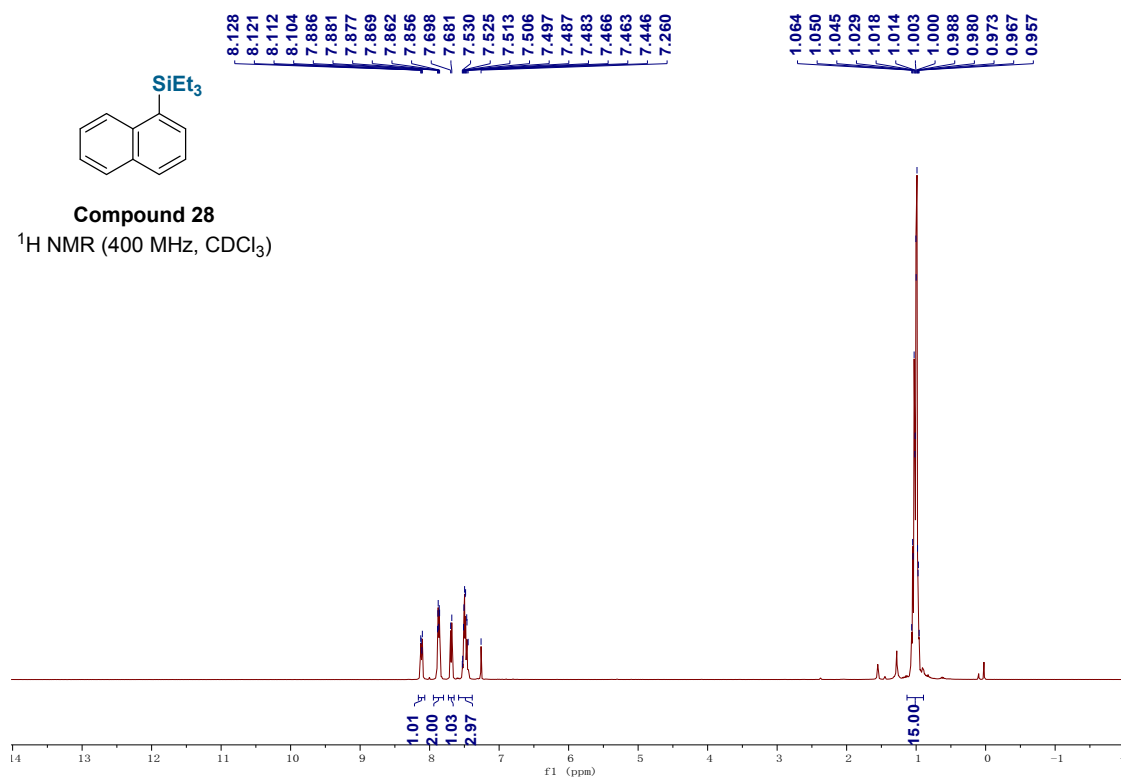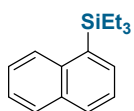
Compound 28

¹³C NMR (100 MHz, CDCl₃)

137.63
135.31
134.60
133.50
129.71
129.20
128.02
125.65
125.36
125.18

77.48
77.16
76.84

7.82
4.63

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2-Methoxy-5-(triethylsilyl)pyridine (29)

SiEt₃
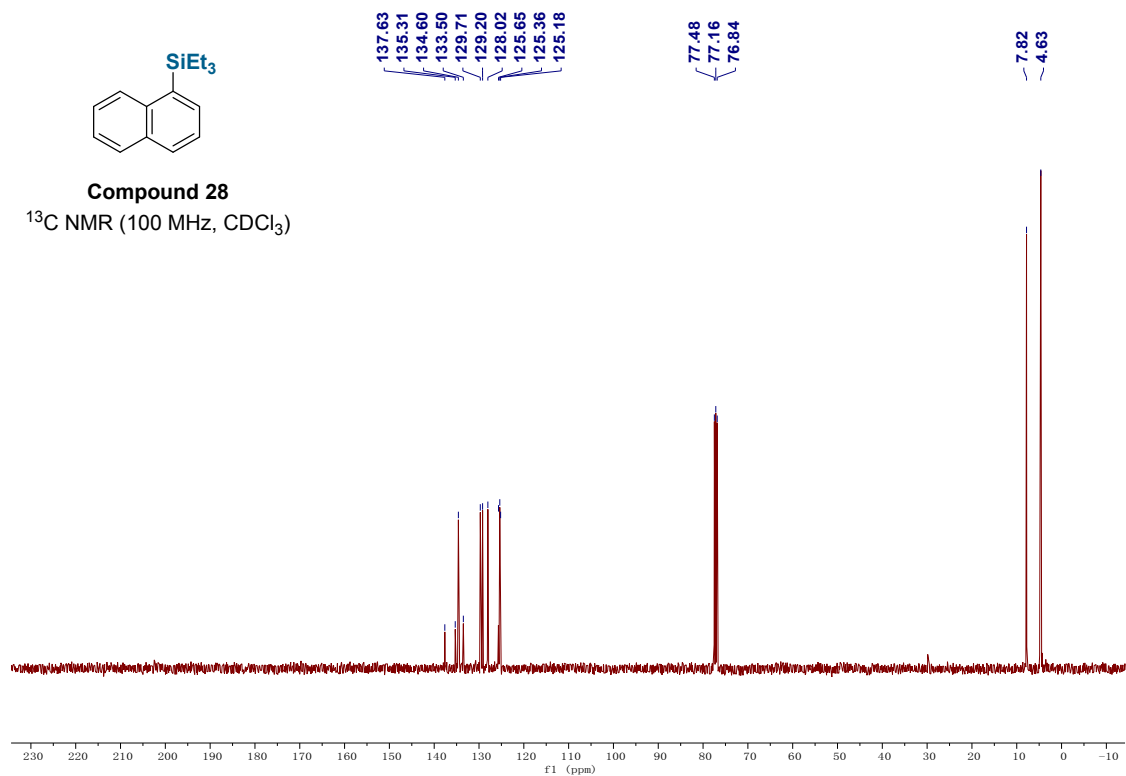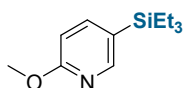
Compound 29

¹H NMR (400 MHz, CDCl₃)

8.218

7.638
7.617
7.260

6.748
6.727

3.934

0.968
0.948
0.929
0.796
0.776
0.756
0.737

0.94 1.00 1.02 3.04 9.10 6.12

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
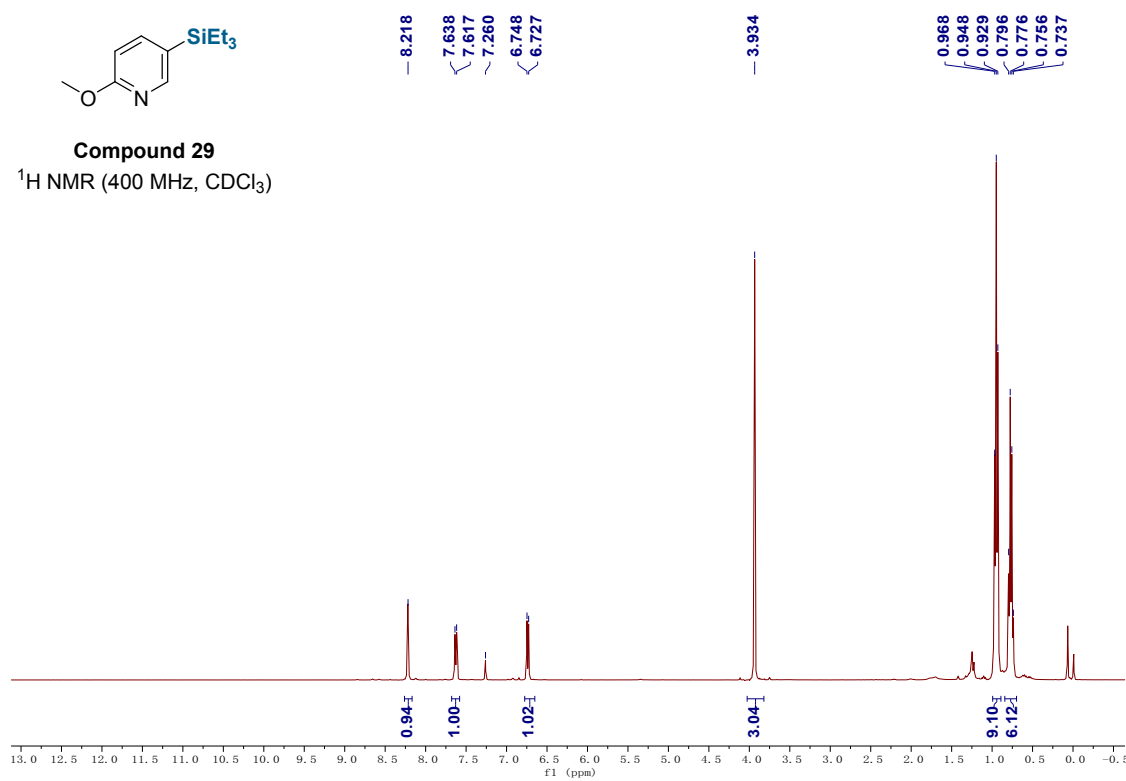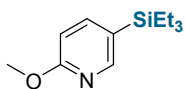
Compound 29
^{13}C NMR (100 MHz, CDCl$_3$)

164.79
152.40
144.32
123.31
110.77
77.48
77.16
76.84
53.31
7.41
3.41

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

4-(Triethylsilyl)isoquinoline (30)

9.236
8.573
8.038
8.017
7.980
7.960
7.720
7.699
7.682
7.615
7.596
7.578
7.260
1.048
1.045
1.034
1.029
1.012
1.001
0.997
0.982
0.978
0.965
0.958
0.950
0.944
0.935
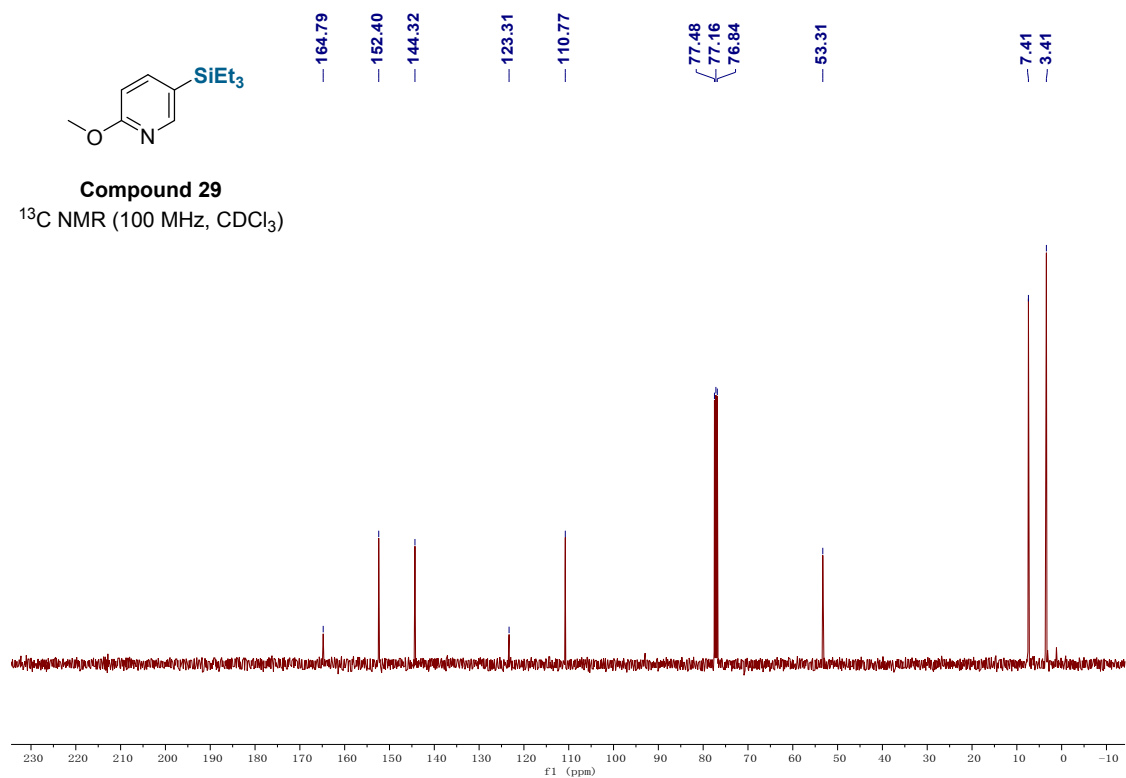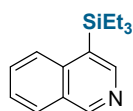
Compound 30
^{1}H NMR (400 MHz, CDCl$_3$)

1.00
1.03
0.97
1.09
1.07
1.02
15.06

12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

SiEt₃

Compound 30
¹³C NMR (100 MHz, CDCl₃)

154.13
149.68
139.99
130.25
128.96
128.26
126.84
126.81
77.48
77.16
76.84
7.65
4.29

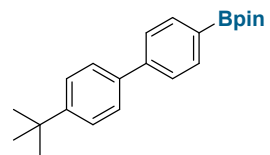## 2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31)

7.950
7.938
7.662
7.650
7.486
7.474
7.462
7.398
7.386
7.375
7.267
1.402

Bpin

Compound 31
¹H NMR (400 MHz, CDCl₃)

2.00
4.04
2.11
1.10
12.12
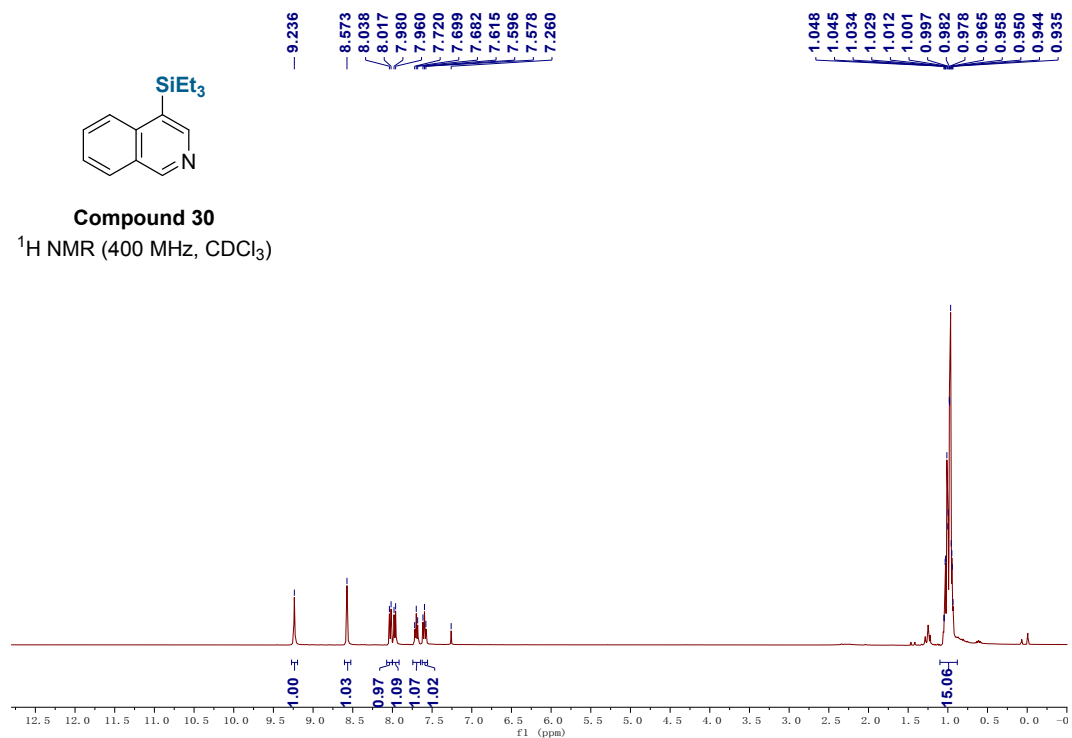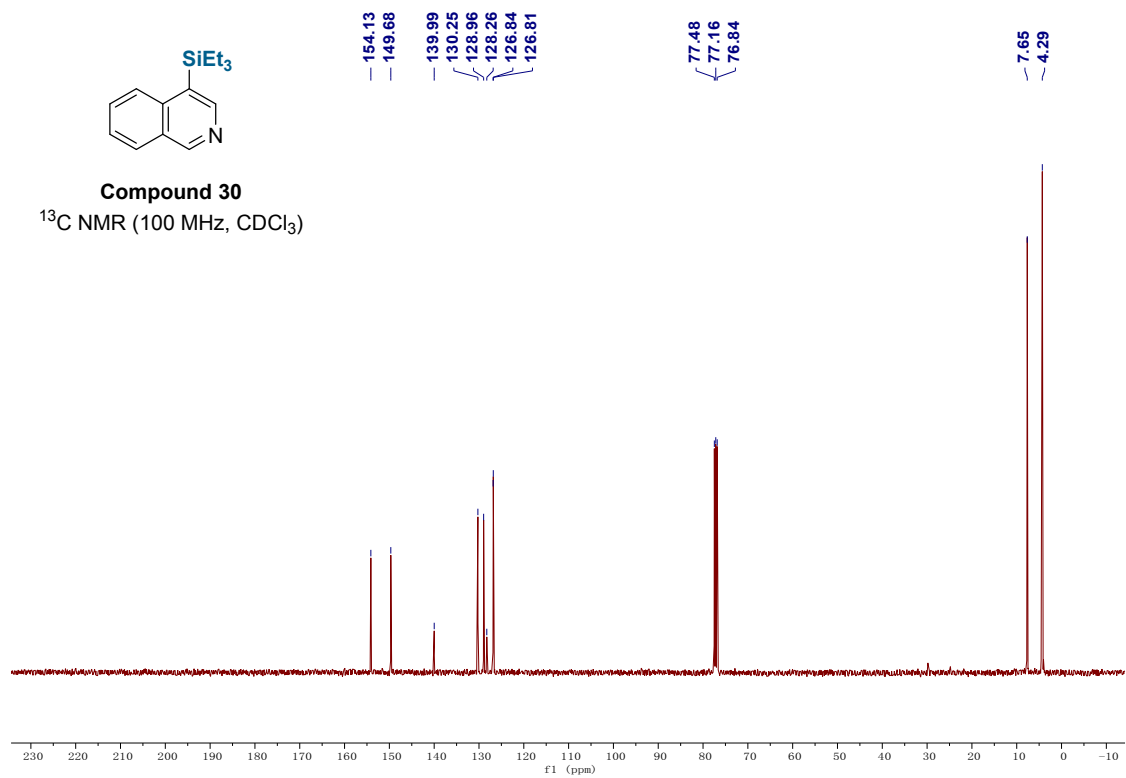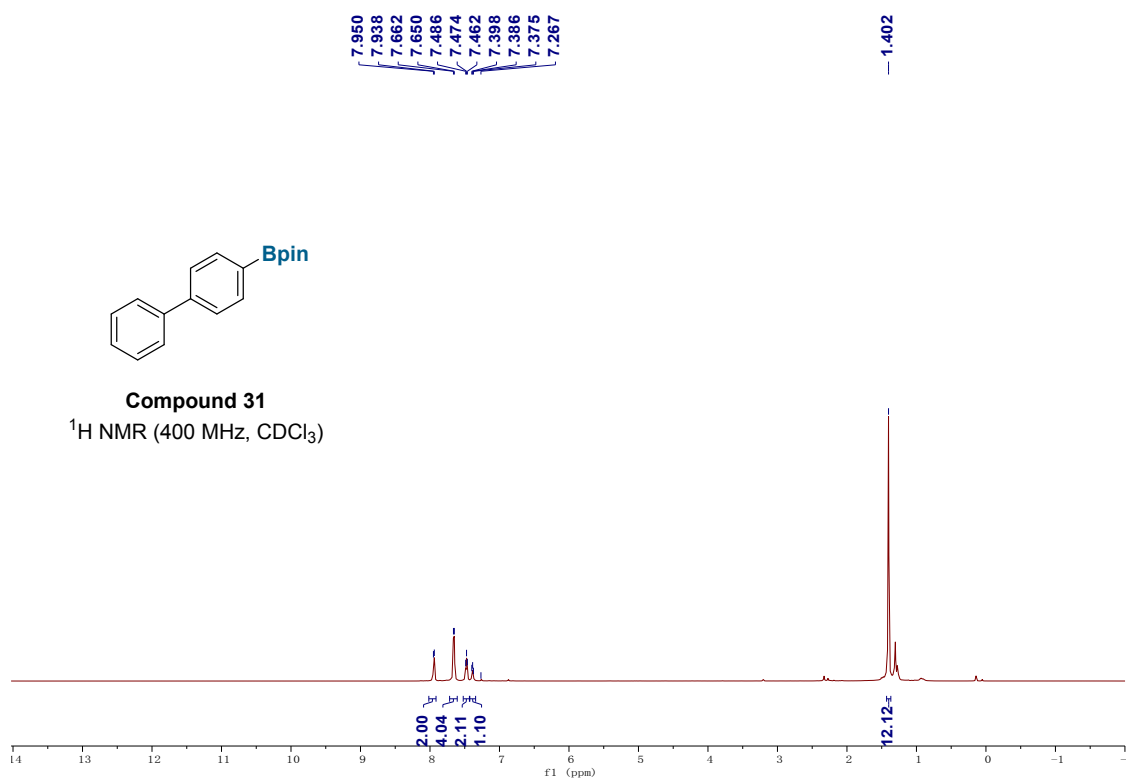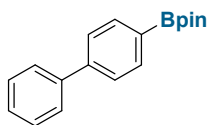
Compound 31

^{13}C NMR (100 MHz, CDCl$_3$)

144.00
141.13
135.38
128.87
127.66
127.33
126.56

83.91
77.37
77.16
76.95

25.00

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

4-Methyl-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (32)

7.914
7.901
7.628
7.616
7.549
7.536
7.274
7.261

2.414

1.384
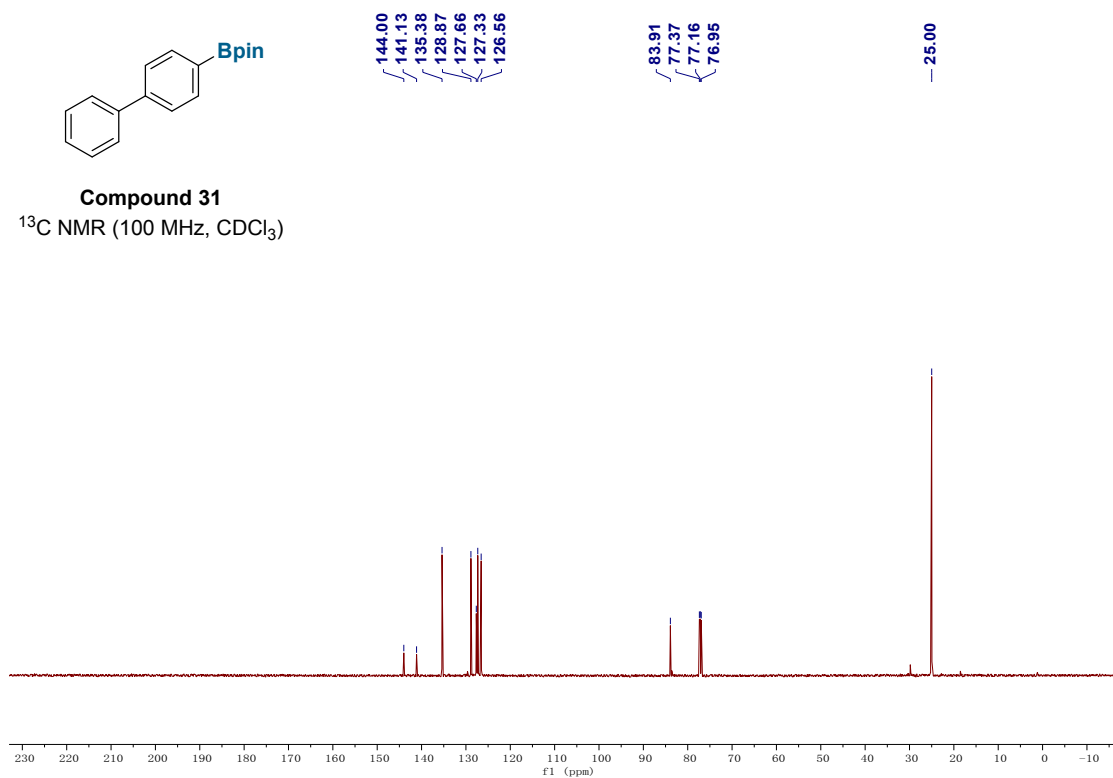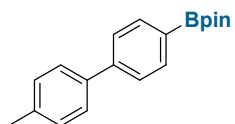
Compound 32

^{1}H NMR (400 MHz, CDCl$_3$)

2.00
2.11
2.12
2.08

3.14

12.46

3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
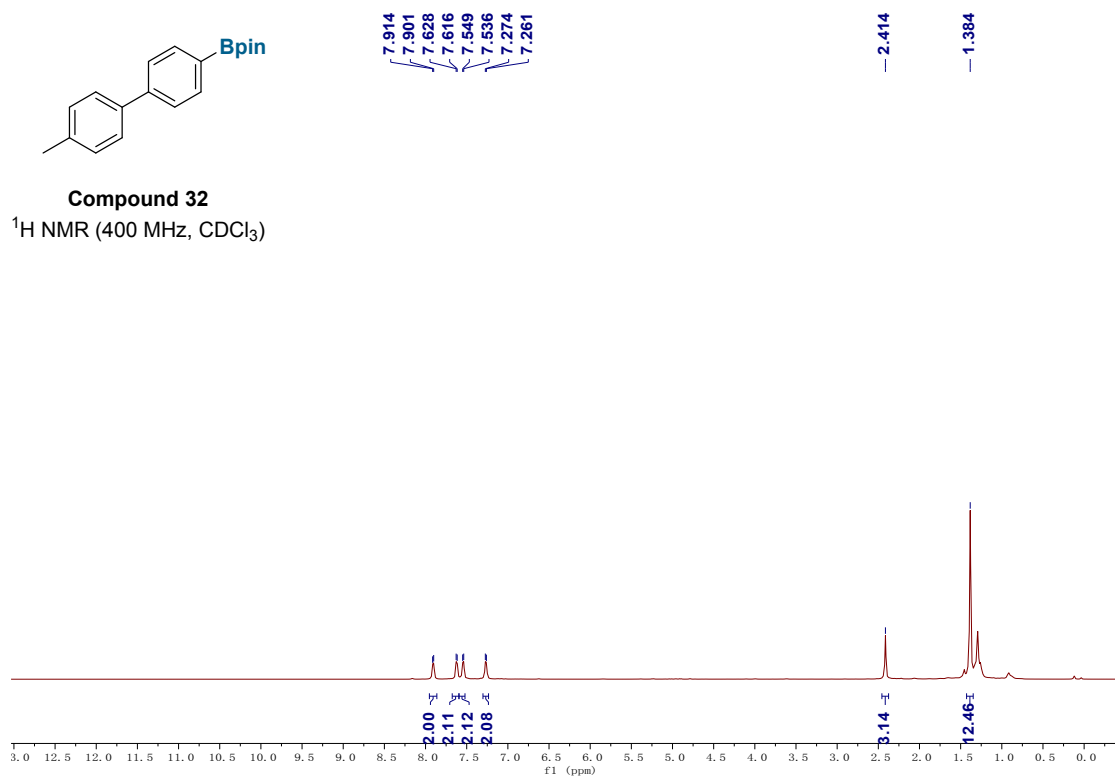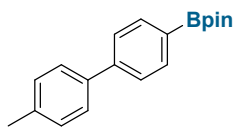
Compound 32

^{13}C NMR (100 MHz, CDCl$_3$)

143.95
138.24
137.49
135.37
129.62
127.17
126.36

83.89
77.37
77.16
76.95

24.99
21.24
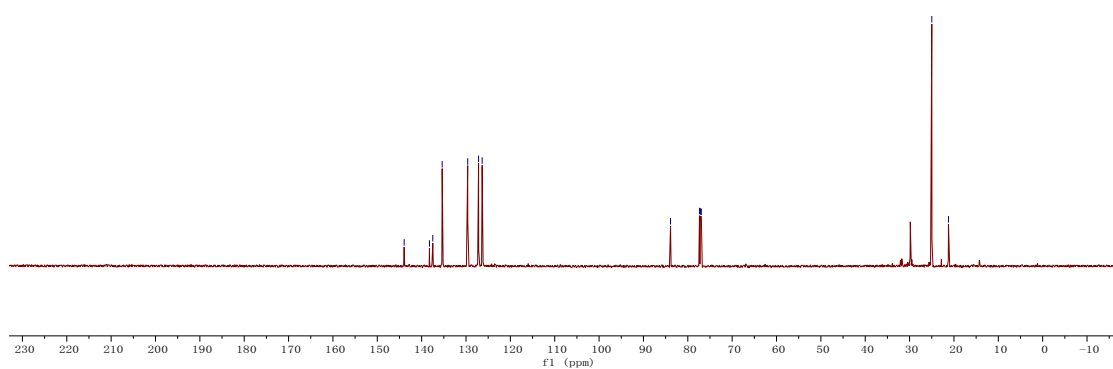
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
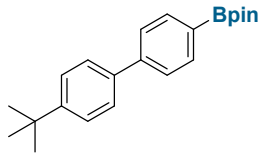
2-(4'-(Tert-Butyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33)

Compound 33

^{1}H NMR (400 MHz, CDCl$_3$)

7.898
7.879
7.632
7.612
7.593
7.572
7.492
7.472
7.260

1.374

2.00
2.16
2.15
2.15

21.39

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)

Compound 33

^{13}C NMR (100 MHz, CDCl$_3$)

150.77
143.85
138.22
135.36
127.00
126.44
125.88

83.92
77.48
77.16
76.84

34.70
31.50
25.02

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

71
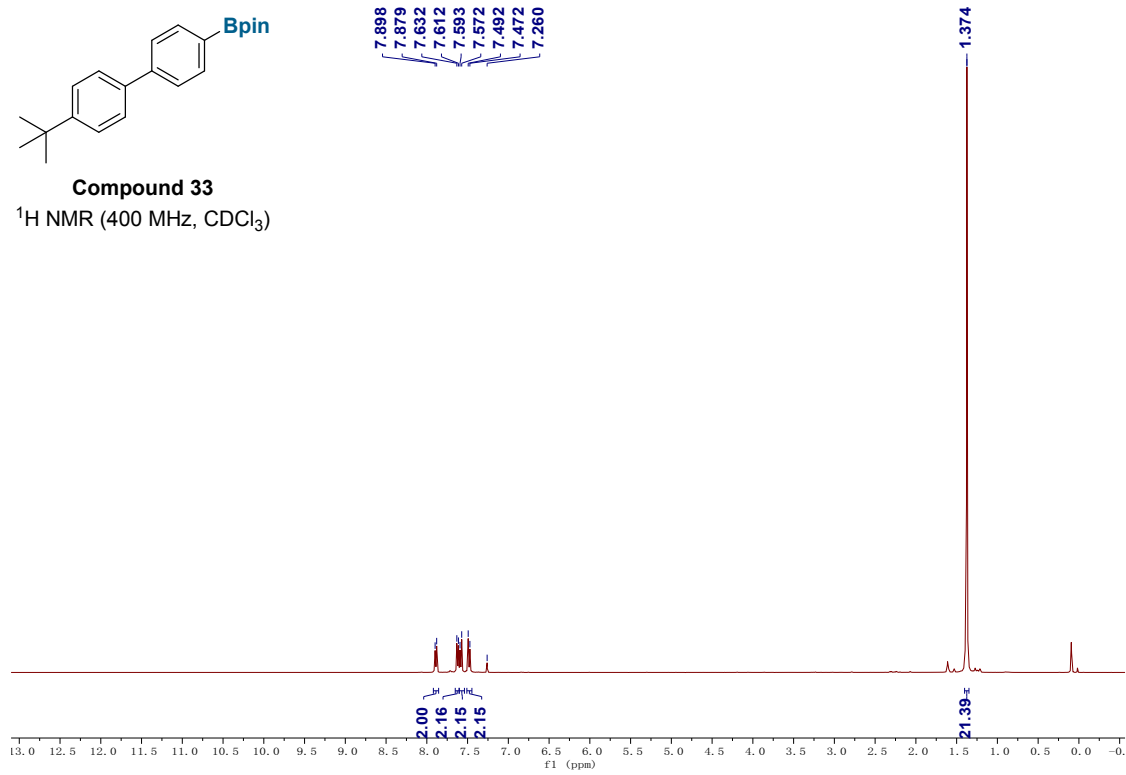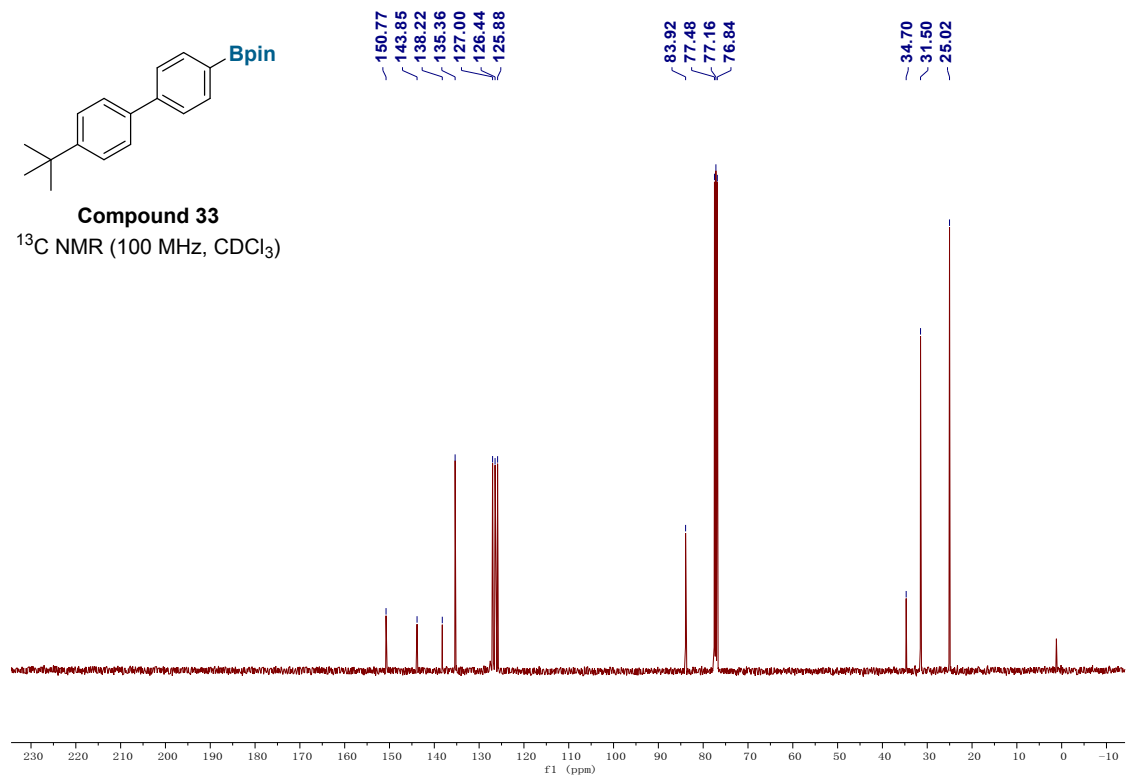
2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34)
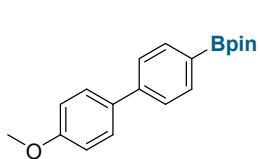
Compound 34

^{1}H NMR (400 MHz, CDCl$_3$)

7.871, 7.851, 7.582, 7.575, 7.570, 7.566, 7.562, 7.558, 7.553, 7.260, 6.992, 6.970 — 3.854 — 1.362
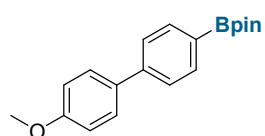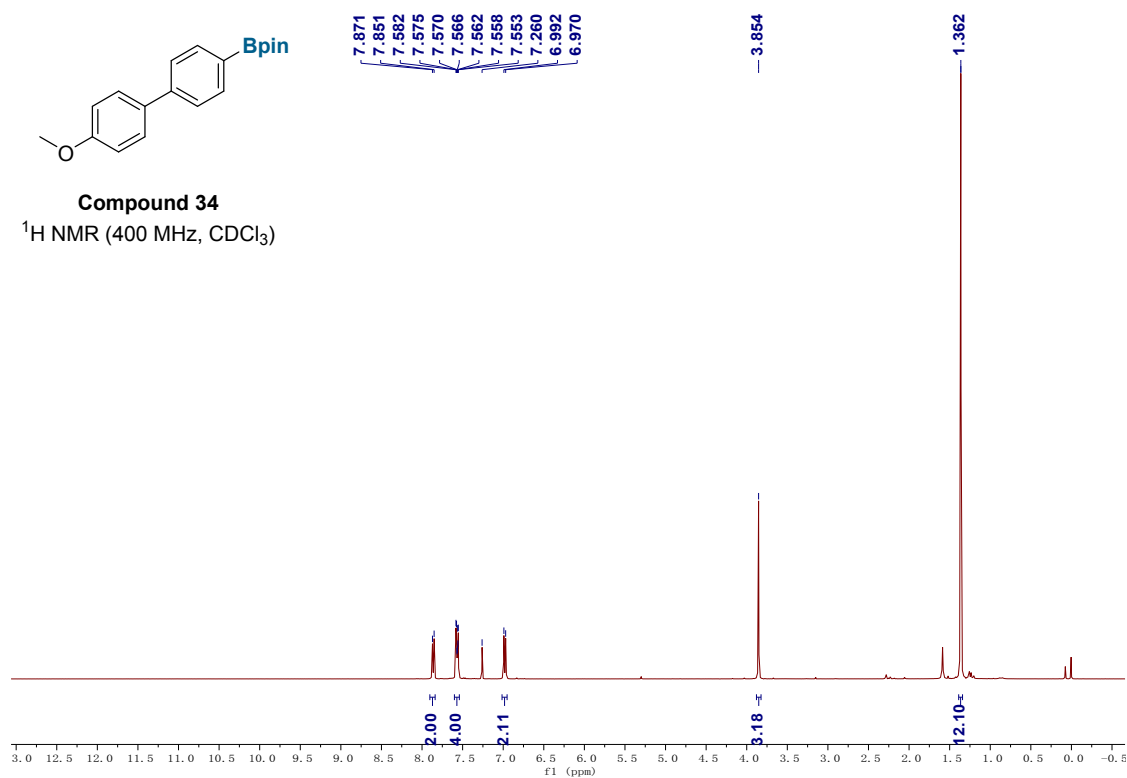
Compound 34

^{13}C NMR (100 MHz, CDCl$_3$)

159.53, 143.61, 135.39, 133.64, 128.40, 126.13, 114.36, 83.92, 77.48, 77.36, 77.16, 76.84, 55.50, 25.02
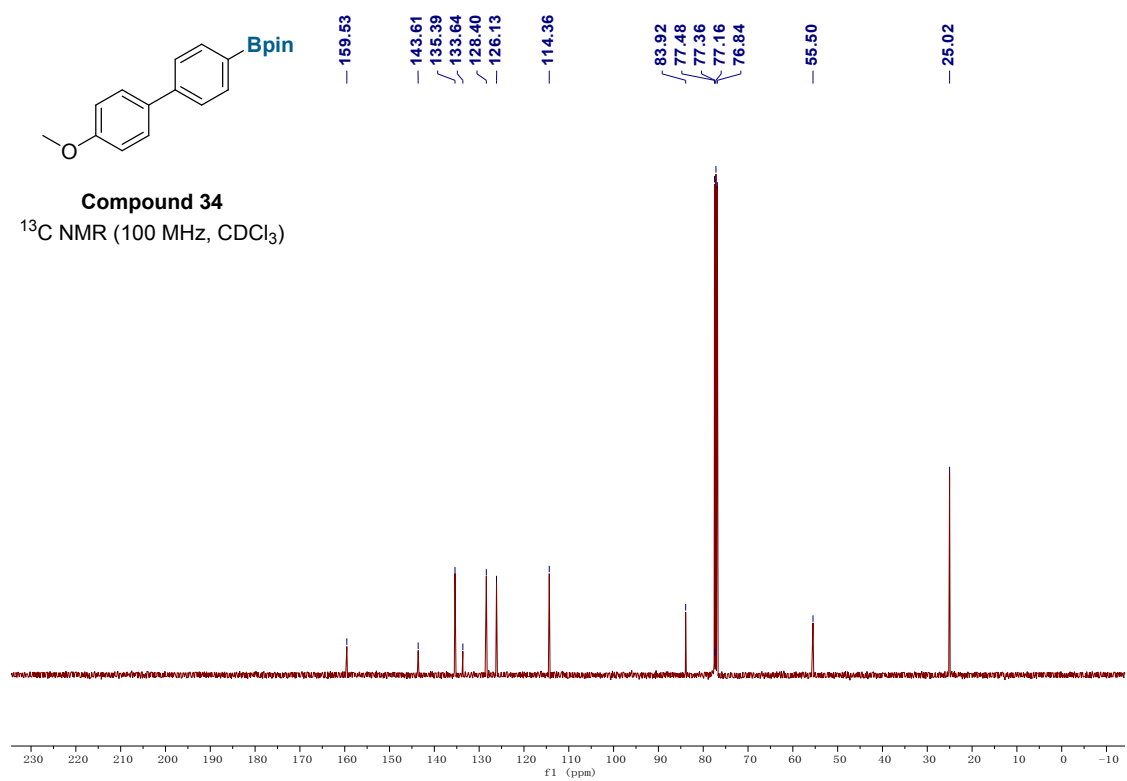
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2′,4′,6′-trimethylbiphenyl (35).
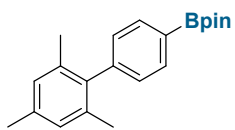
Compound 35
^{1}H NMR (400 MHz, CDCl$_3$)
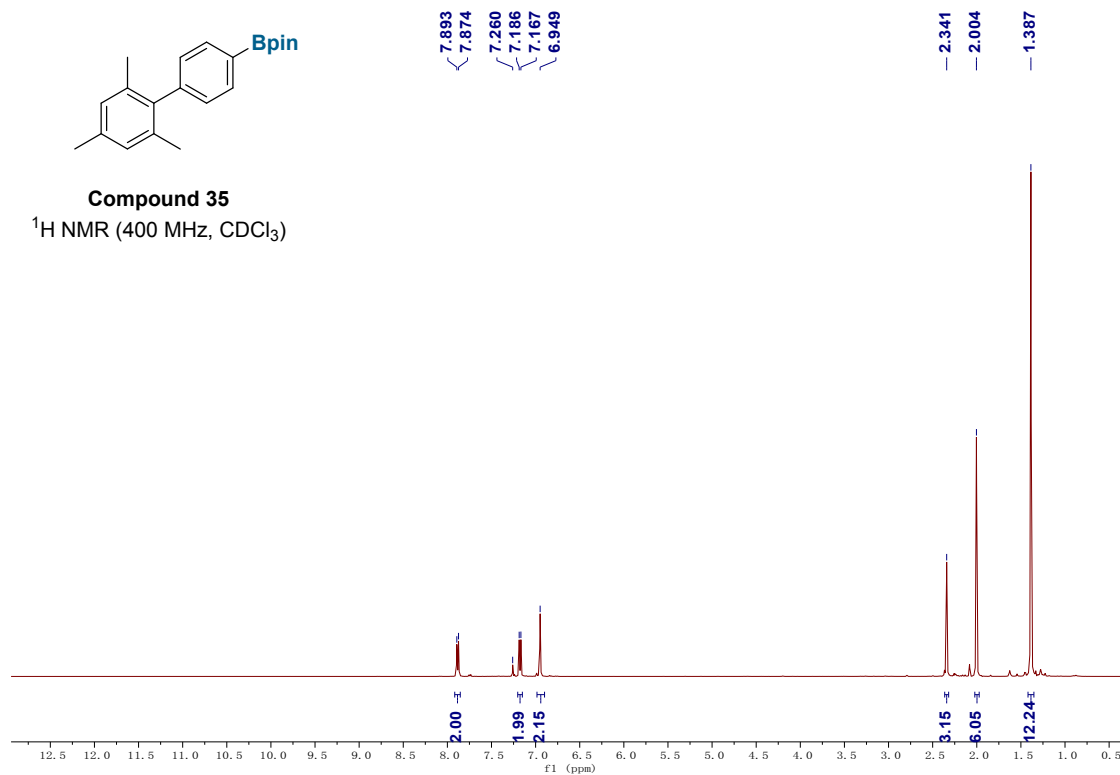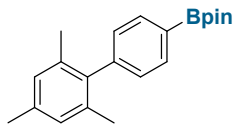
Compound 35

^{13}C NMR (100 MHz, CDCl$_3$)

144.39
139.06
136.74
135.84
134.96
128.91
128.18

83.91
77.48
77.16
76.84

25.06
21.16
20.83
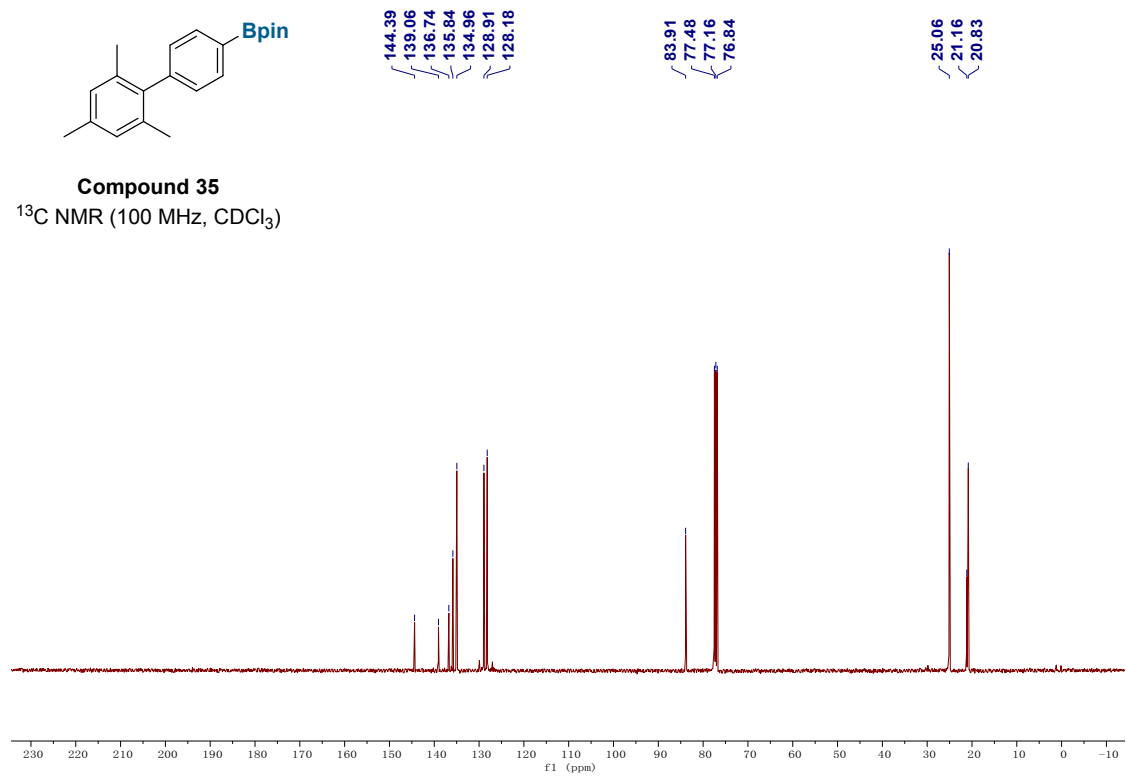
4-Phenoxy-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (36)
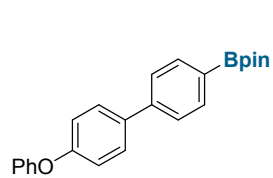
Compound 36

^{1}H NMR (400 MHz, CDCl$_3$)

7.897
7.878
7.603
7.582
7.386
7.366
7.347
7.260
7.152
7.134
7.115
7.096
7.075
7.058

1.373

2.03
4.11
2.00
0.95
3.90

12.20

Compound 36

^{13}C NMR (100 MHz, CDCl$_3$)

157.23
157.20
143.31
136.13
135.43
135.39
129.94
128.66
126.31
123.56
119.17
83.96
77.48
77.16
76.84
25.02
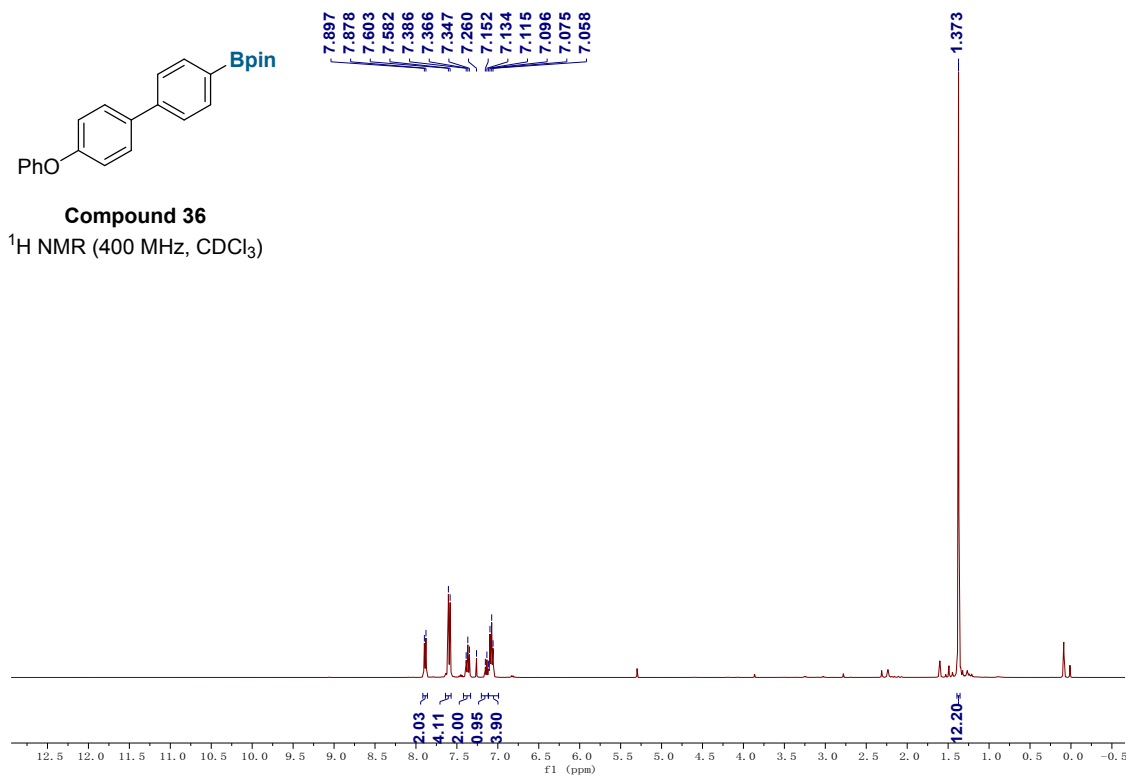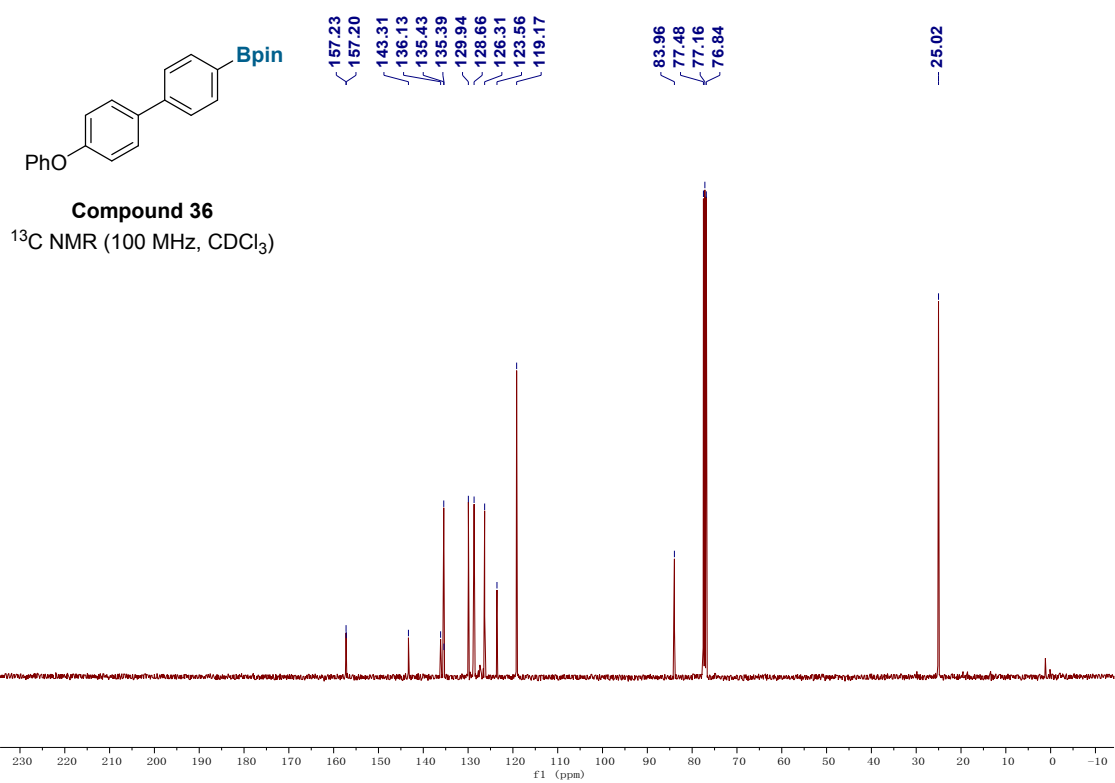
3,4-Methylenedioxy-4′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (37)
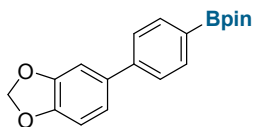
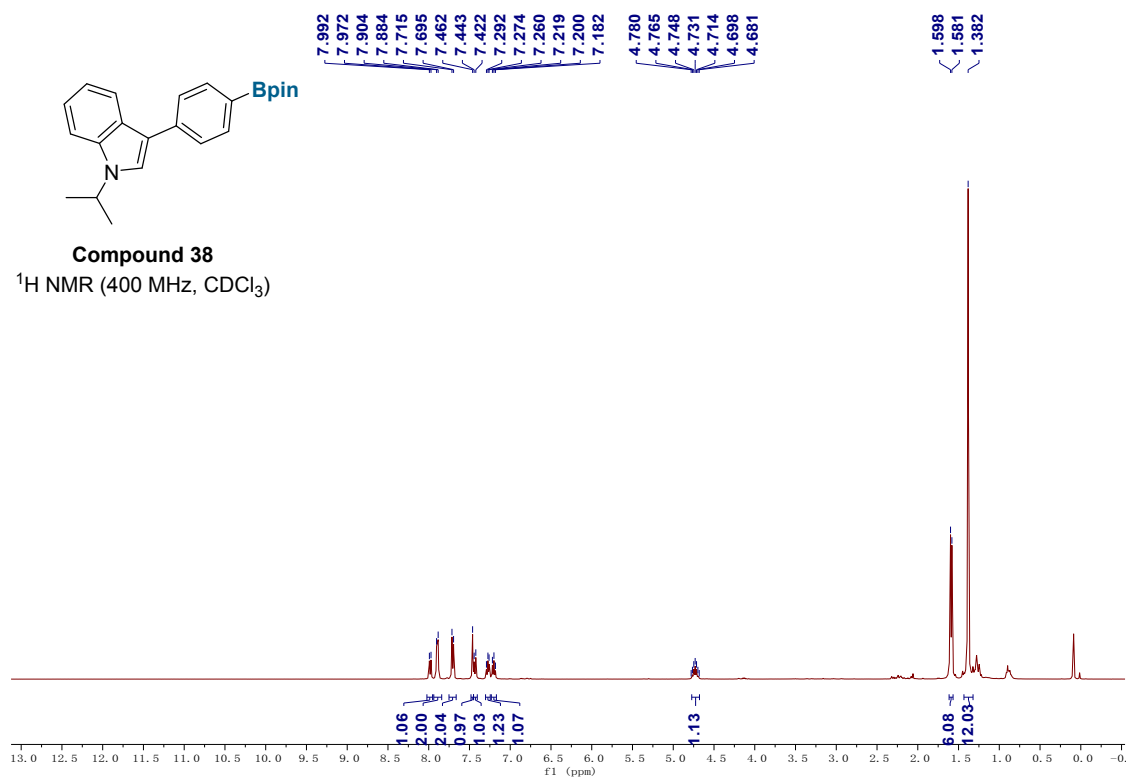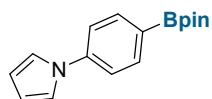**Compound 37**
^{1}H NMR (400 MHz, CDCl$_3$)
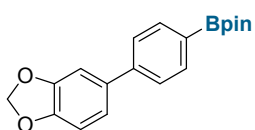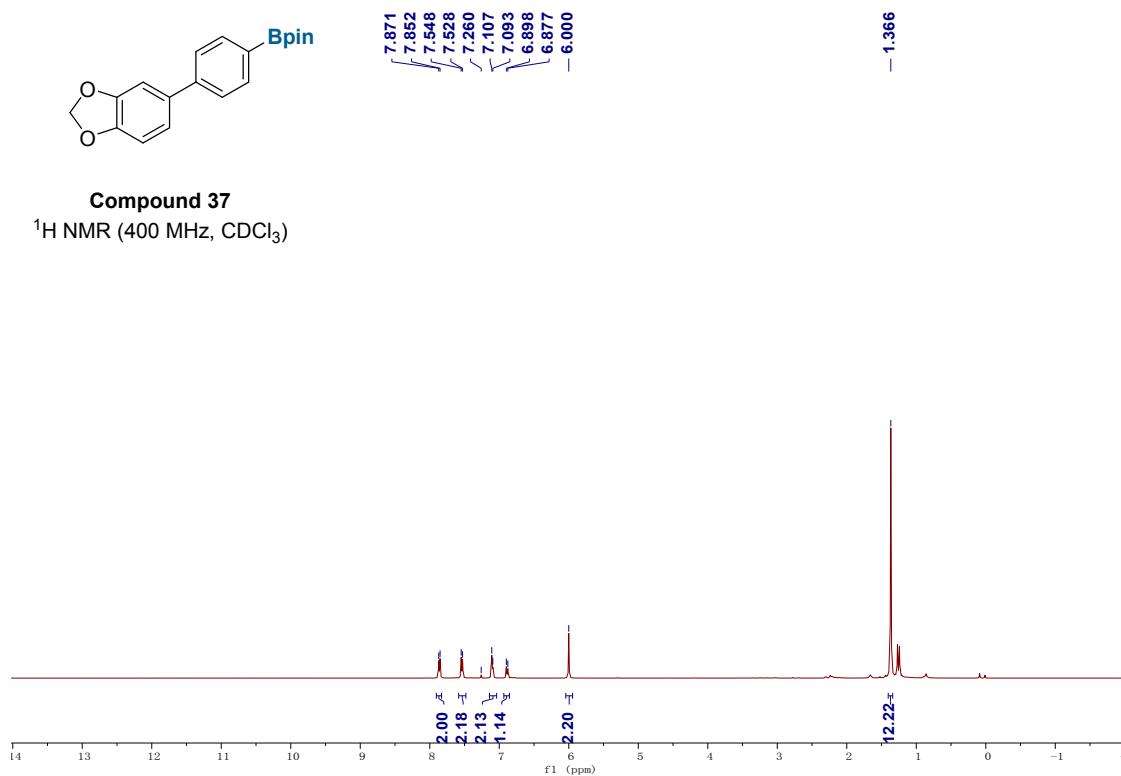
Compound 37
^{13}C NMR (100 MHz, CDCl$_3$)
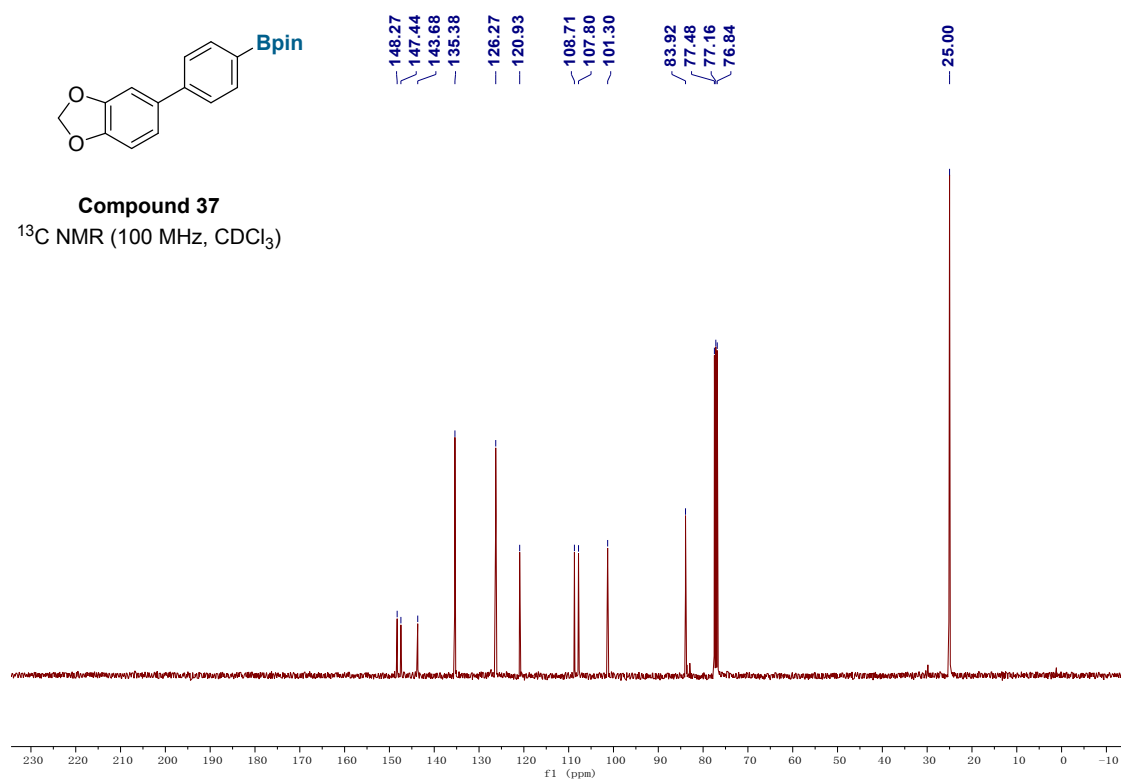
1-Isopropyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)indole (38)

Compound 38

^{1}H NMR (400 MHz, CDCl$_3$)
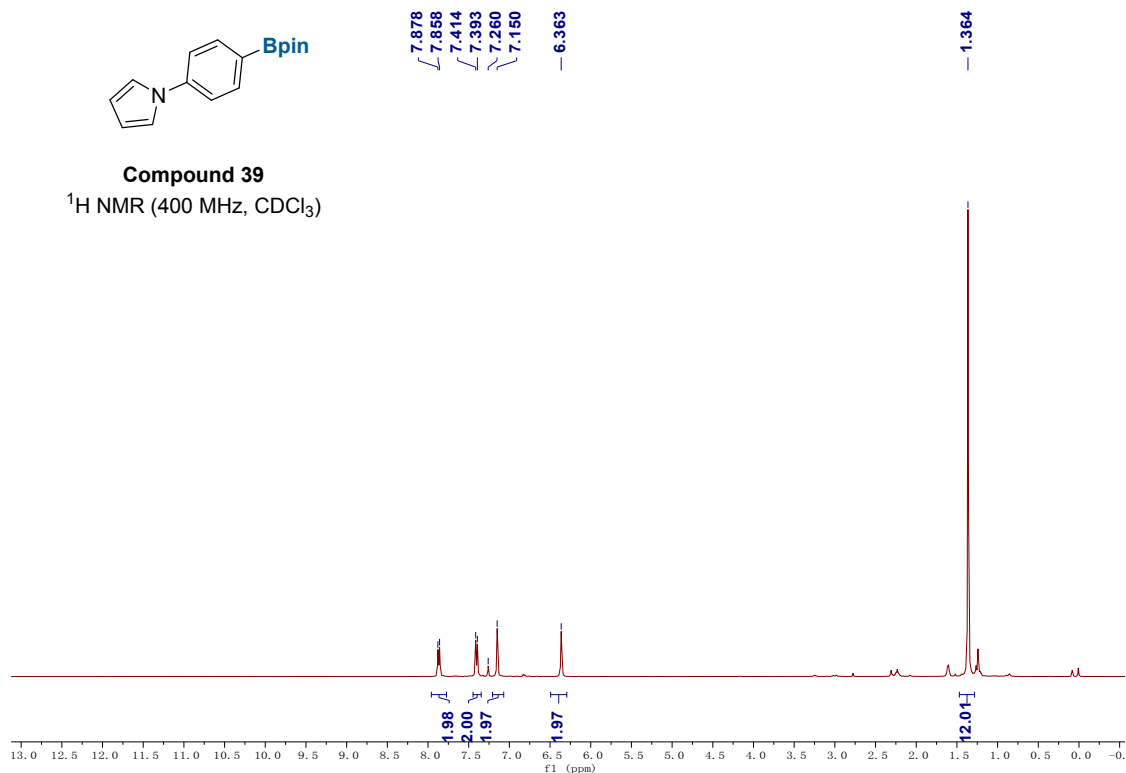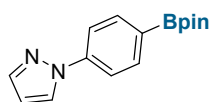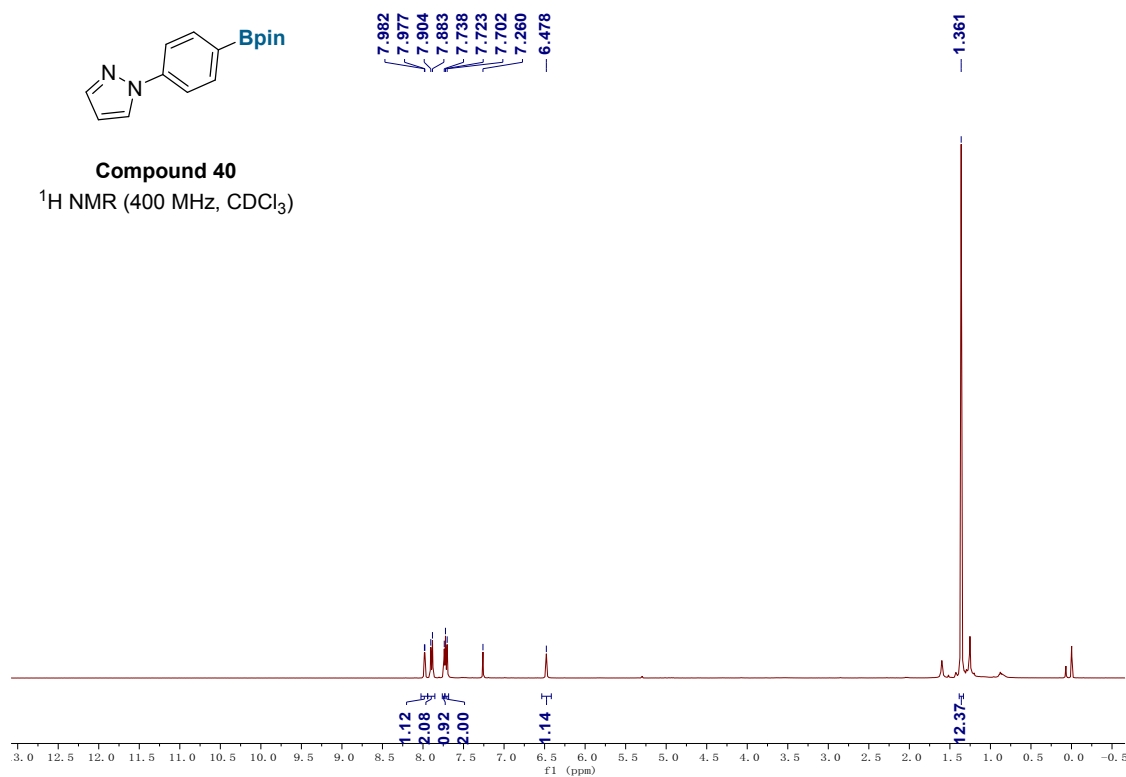
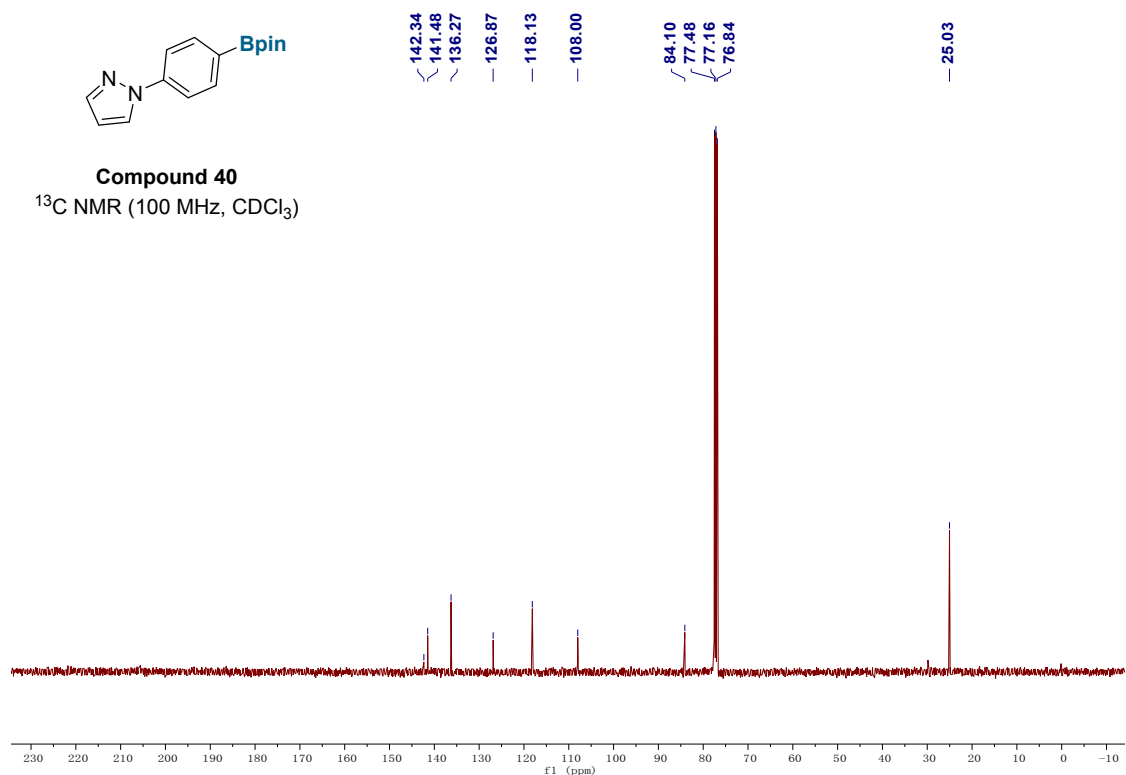**Compound 38**

^{13}C NMR (100 MHz, CDCl$_3$)
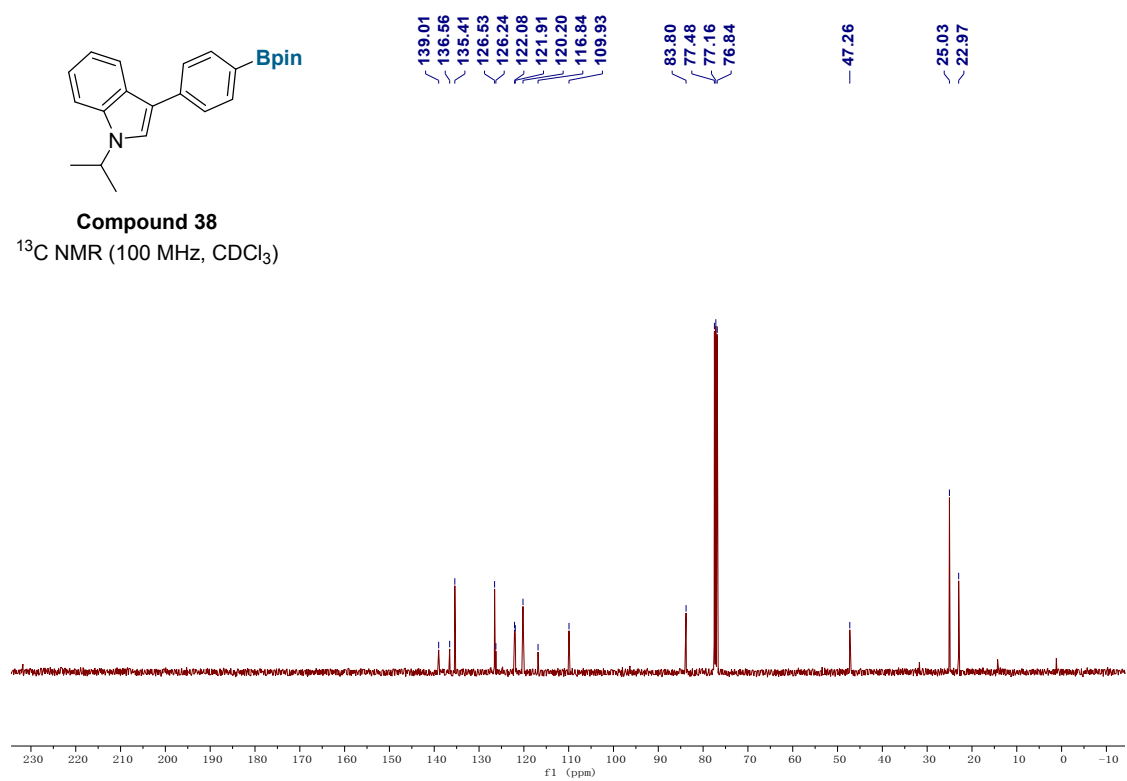
N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrole (39)
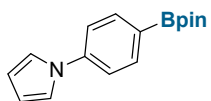
Compound 39

^{1}H NMR (400 MHz, CDCl$_3$)

7.878
7.858
7.414
7.393
7.260
7.150
6.363
1.364

Compound 39

^{13}C NMR (100 MHz, CDCl$_3$)

142.97
136.40
119.37
119.21
110.86
84.04
77.48
77.16
76.84
25.01

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-pyrazole (40)

Bpin

7.982
7.977
7.904
7.883
7.738
7.723
7.702
7.260
6.478

1.361
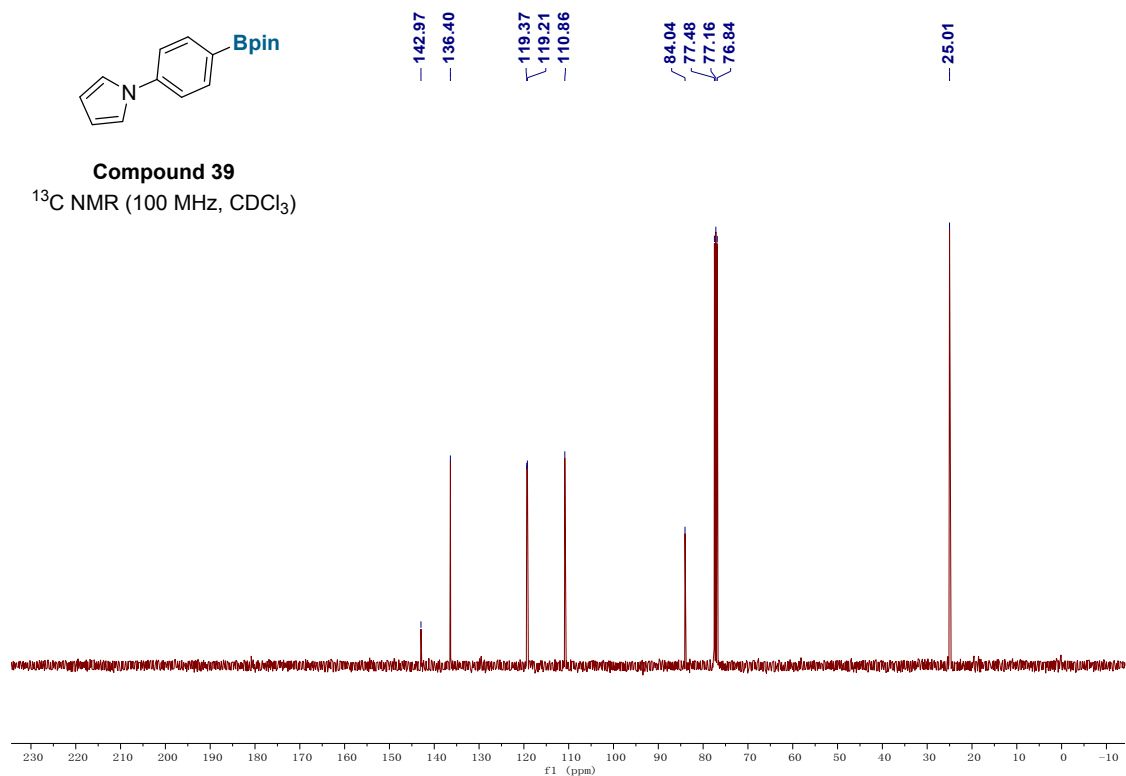
Compound 40

^{1}H NMR (400 MHz, CDCl$_3$)

1.12
2.08
0.92
2.00
1.14
12.37

Bpin

142.34
141.48
136.27
126.87
118.13
108.00
84.10
77.48
77.16
76.84
25.03

Compound 40
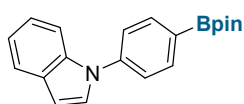
^{13}C NMR (100 MHz, CDCl$_3$)

1-(4-(4,4,5,5- Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-Indole (41)

Compound 41

^{1}H NMR (400 MHz, CDCl$_3$)

7.992, 7.972, 7.708, 7.689, 7.642, 7.621, 7.552, 7.532, 7.383, 7.375, 7.265, 7.249, 7.228, 7.207, 7.188, 7.170, 6.710, 6.703

1.391

2.02, 1.09, 1.08, 2.03, 1.04, 2.28, 1.00

12.00
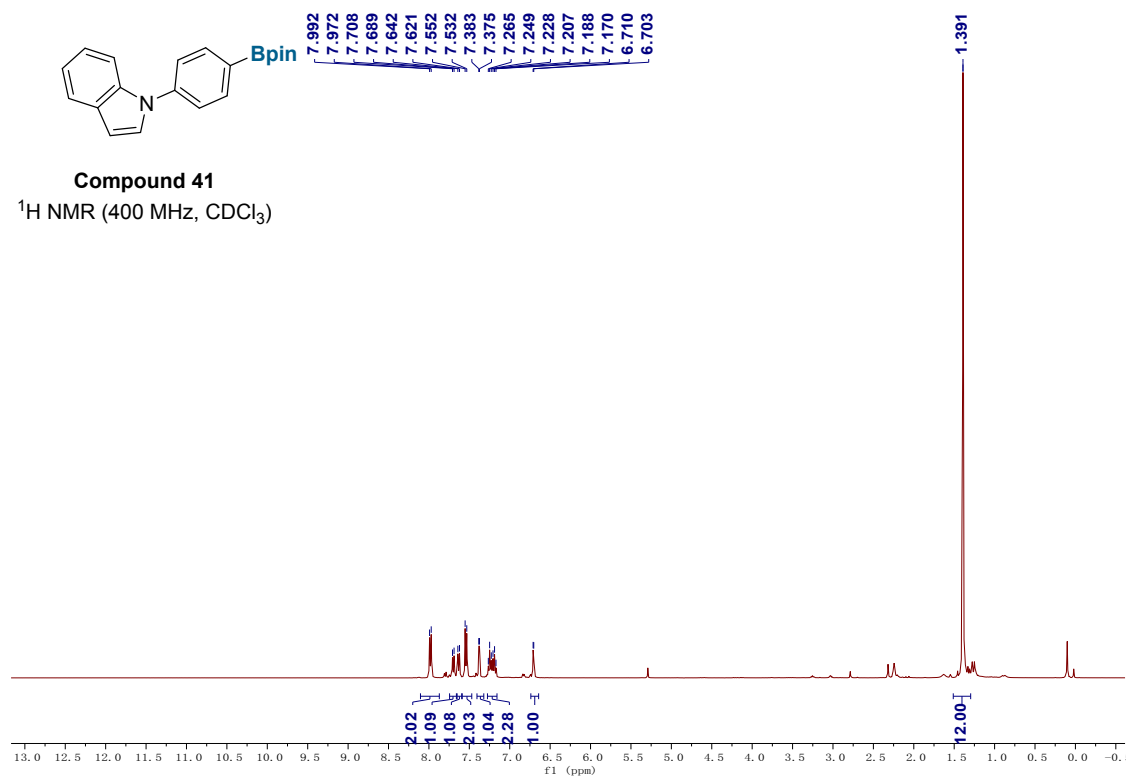
Compound 41

^{13}C NMR (100 MHz, CDCl$_3$)

142.41, 136.37, 135.69, 129.66, 128.28, 127.84, 124.74, 123.27, 122.62, 121.31, 120.66, 110.76

104.15

84.13, 77.48, 77.16, 76.84

25.03

80

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (42)

Bpin

8.409
7.916
7.903
7.884
7.871
7.855
7.842
7.539
7.527
7.514
7.503
7.490
7.478
7.260

1.413
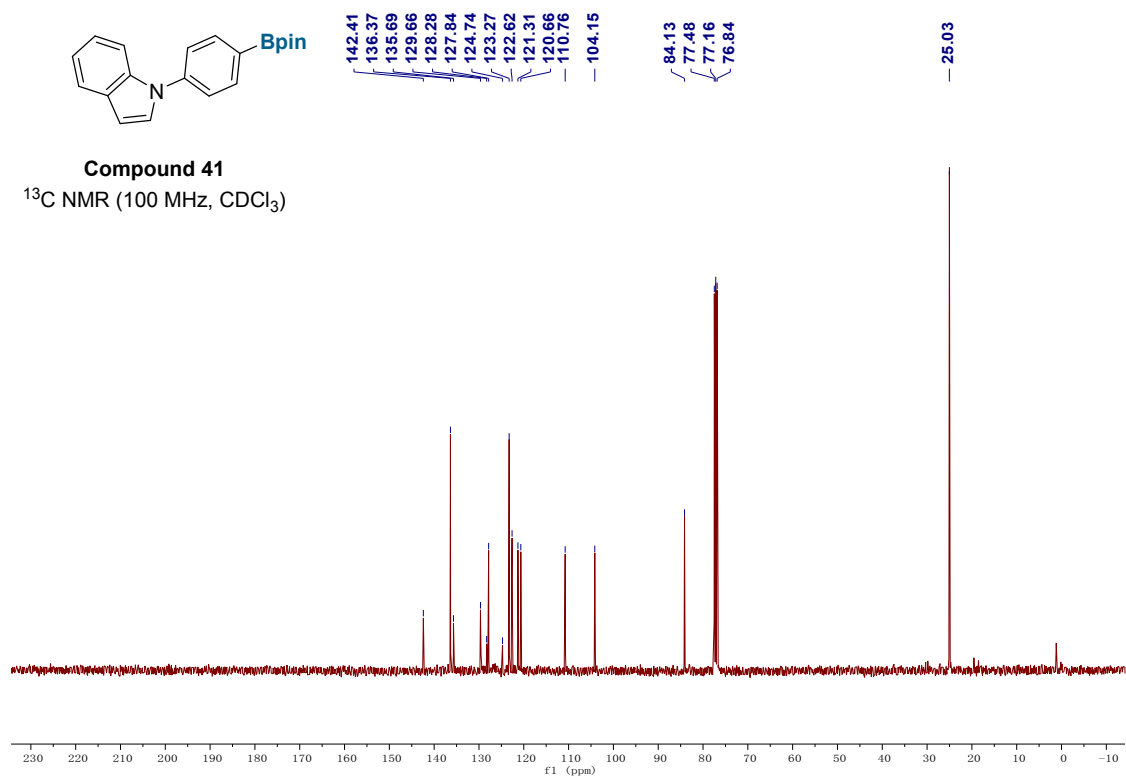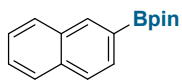
Compound 42

^{1}H NMR (400 MHz, CDCl$_3$)

1.00

4.01

2.02

12.08

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

Bpin

Compound 42

^{13}C NMR (100 MHz, CDCl$_3$)
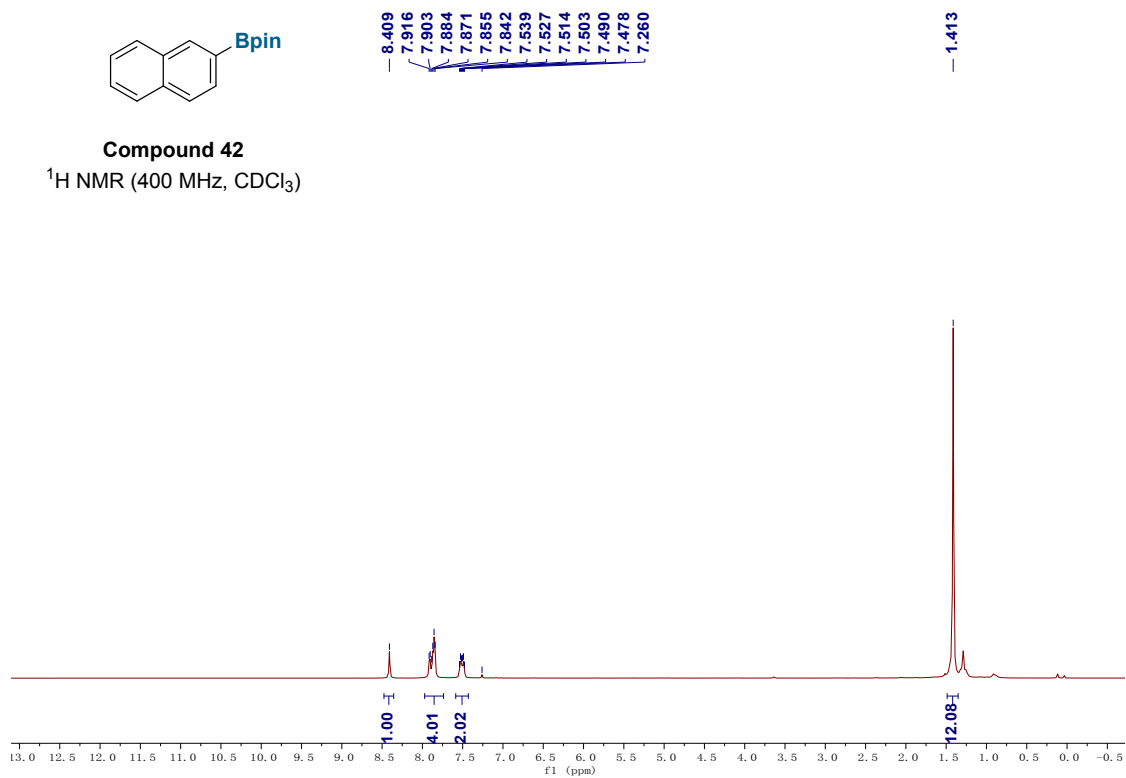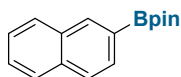
136.38
135.17
132.96
130.54
128.78
127.84
127.09
125.92

84.04
77.37
77.16
76.95

25.05

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (43)

Bpin
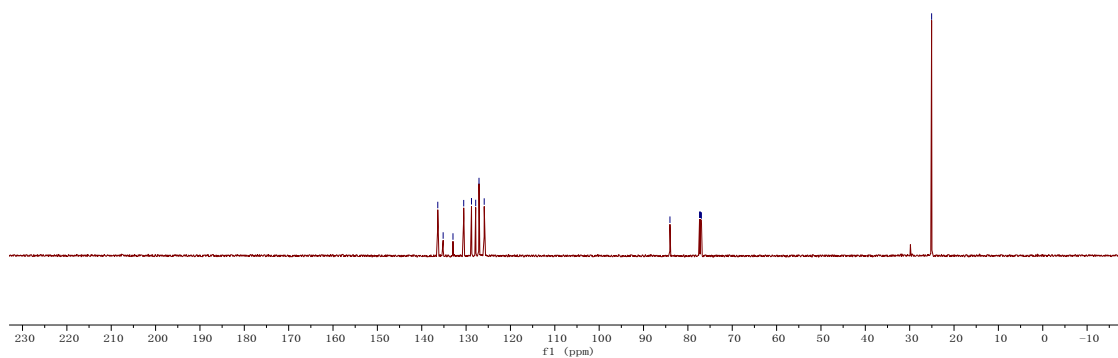
Compound 43
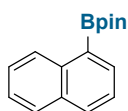
^{1}H NMR (400 MHz, CDCl$_3$)

8.863
8.849
8.836
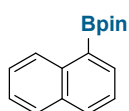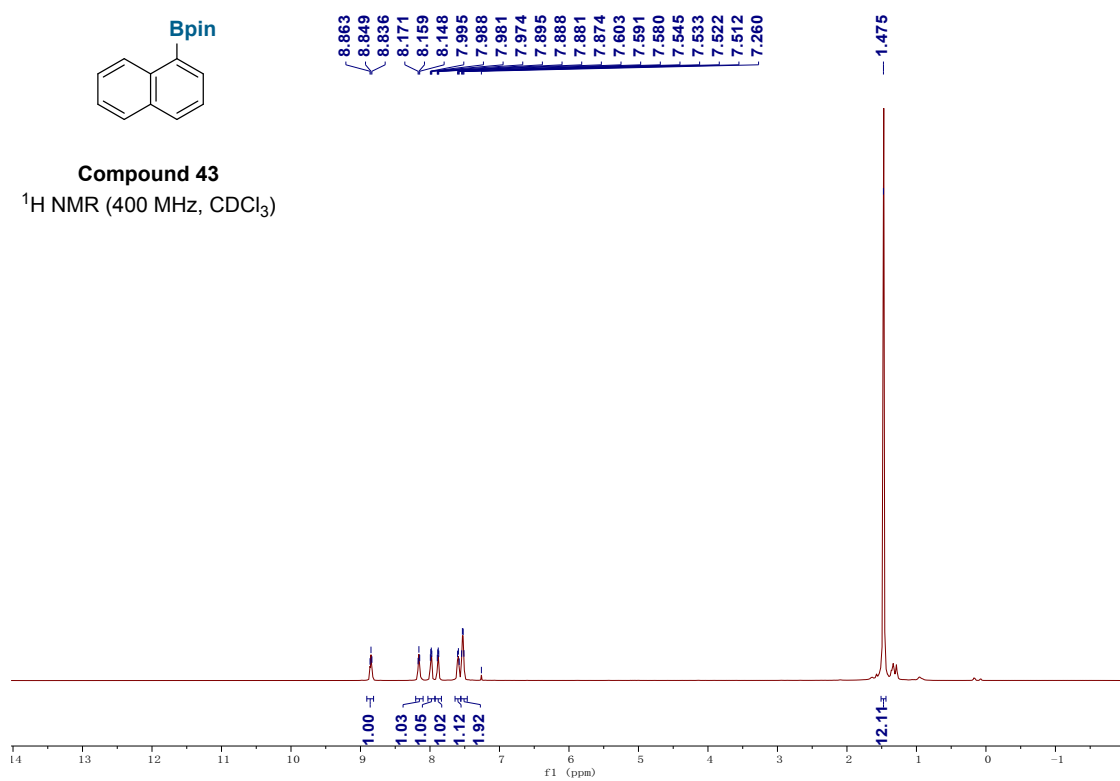8.171
8.159
8.148
7.995
7.988
7.981
7.974
7.895
7.888
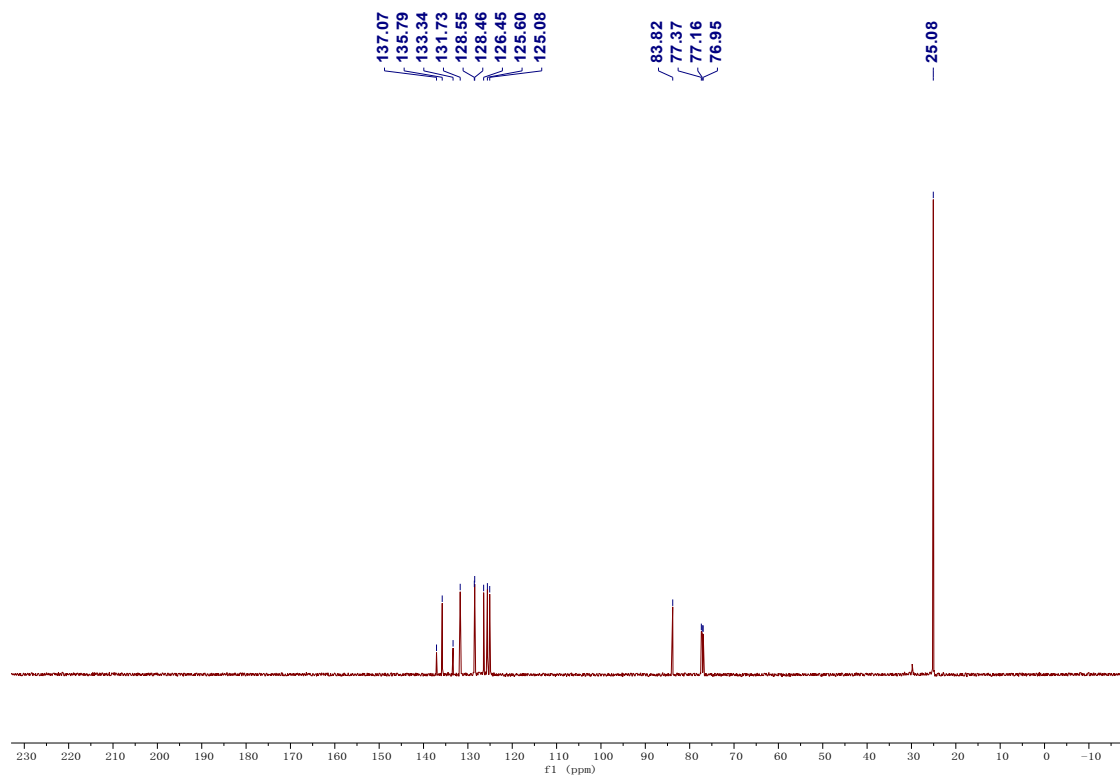7.881
7.874
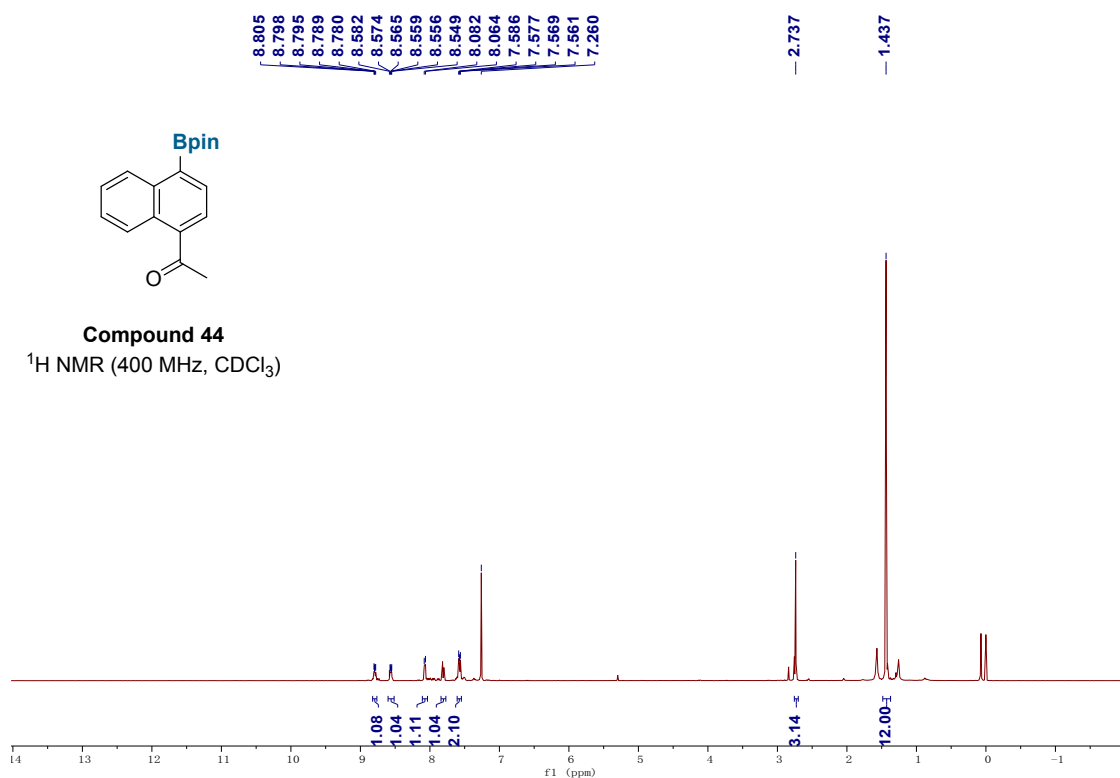7.603
7.591
7.580
7.545
7.533
7.522
7.512
7.260

1.475

1.00
1.03
1.05
1.02
1.12
1.92

12.11

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

Bpin

Compound 43

137.07
135.79
133.34
131.73
128.55
128.46
126.45
125.60
125.08

83.82
77.37
77.16
76.95

25.08

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
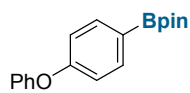
1-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-naphthalenyl]ethanone (44)

8.805
8.798
8.795
8.789
8.780
8.582
8.574
8.565
8.559
8.556
8.549
8.082
8.064
7.586
7.577
7.569
7.561
7.260

2.737

1.437

Bpin

Compound 44
^{1}H NMR (400 MHz, CDCl$_3$)

1.08
1.04
1.11
1.04
2.10

3.14

12.00

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

83

4,4,5,5-Tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane (45)

Compound 45

¹H NMR (400 MHz, CDCl₃)

7.799, 7.778, 7.372, 7.351, 7.332, 7.260, 7.152, 7.133, 7.115, 7.045, 7.024, 6.999, 6.978

1.347

2.00, 2.18, 1.16, 2.11, 2.18

12.17
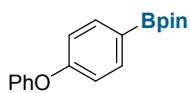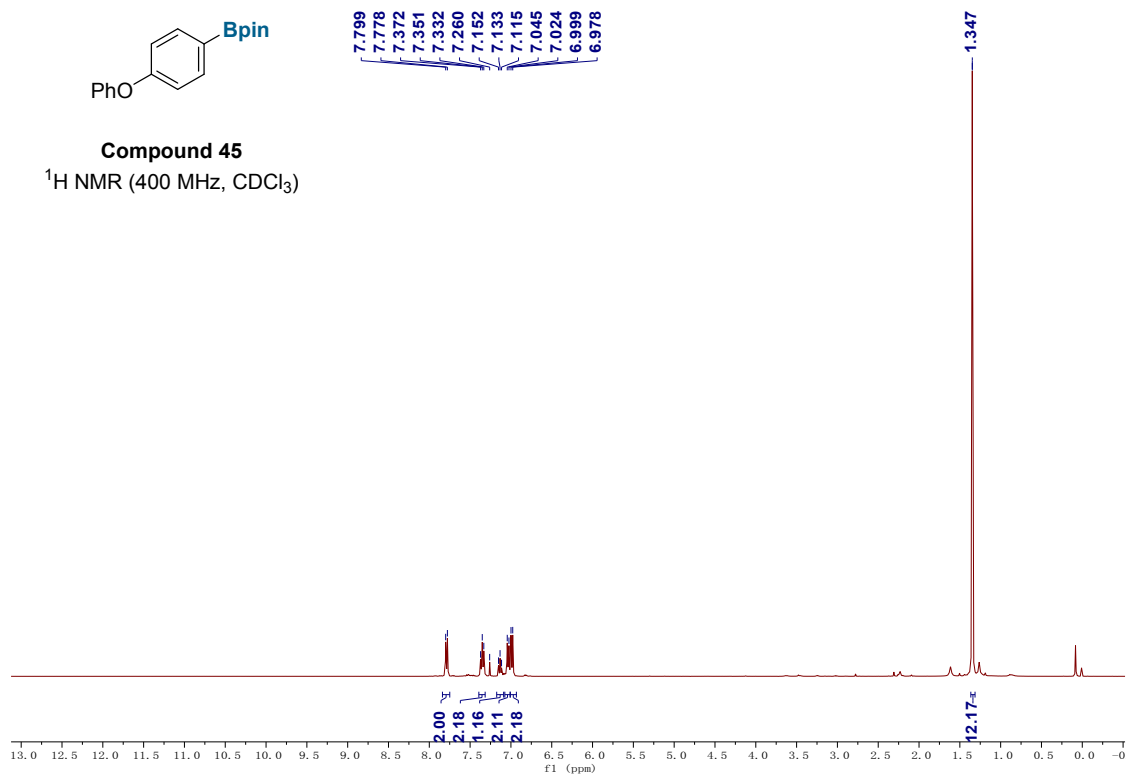
Compound 45

¹³C NMR (100 MHz, CDCl₃)

160.33, 156.68

136.77, 129.94, 123.80, 119.60, 117.81

83.88, 77.48, 77.16, 76.84

25.00

2-(4-(benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46)

7.765 7.743 7.439 7.421 7.397 7.379 7.361 7.336 7.318 7.260 6.984 6.962   5.096   1.332
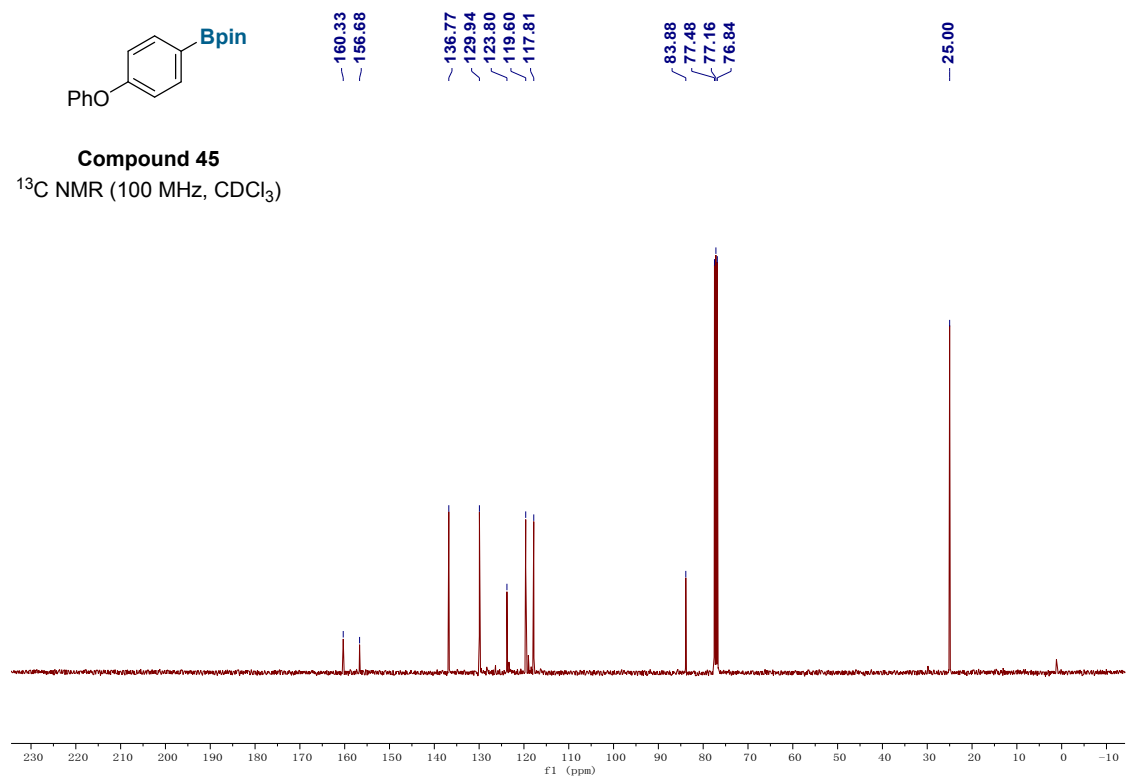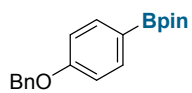
Compound 46
^{1}H NMR (400 MHz, CDCl$_3$)

2.05 2.14 2.23 1.20 2.13   2.00   12.23

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)
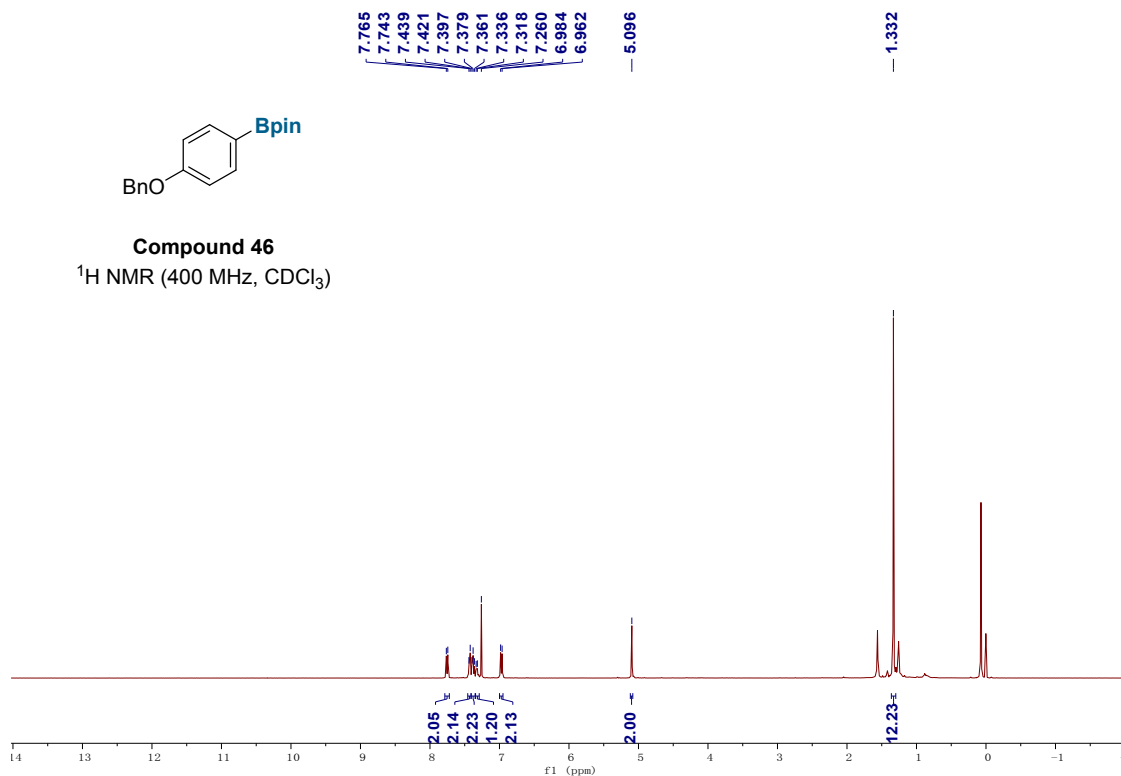
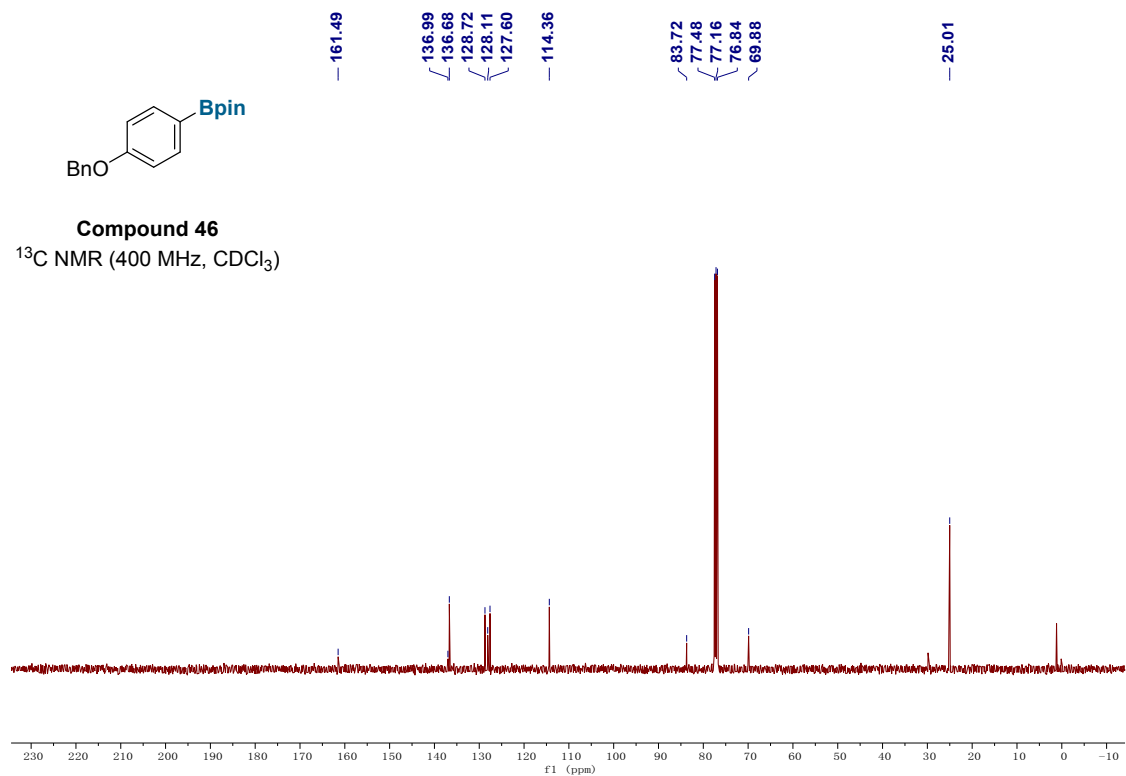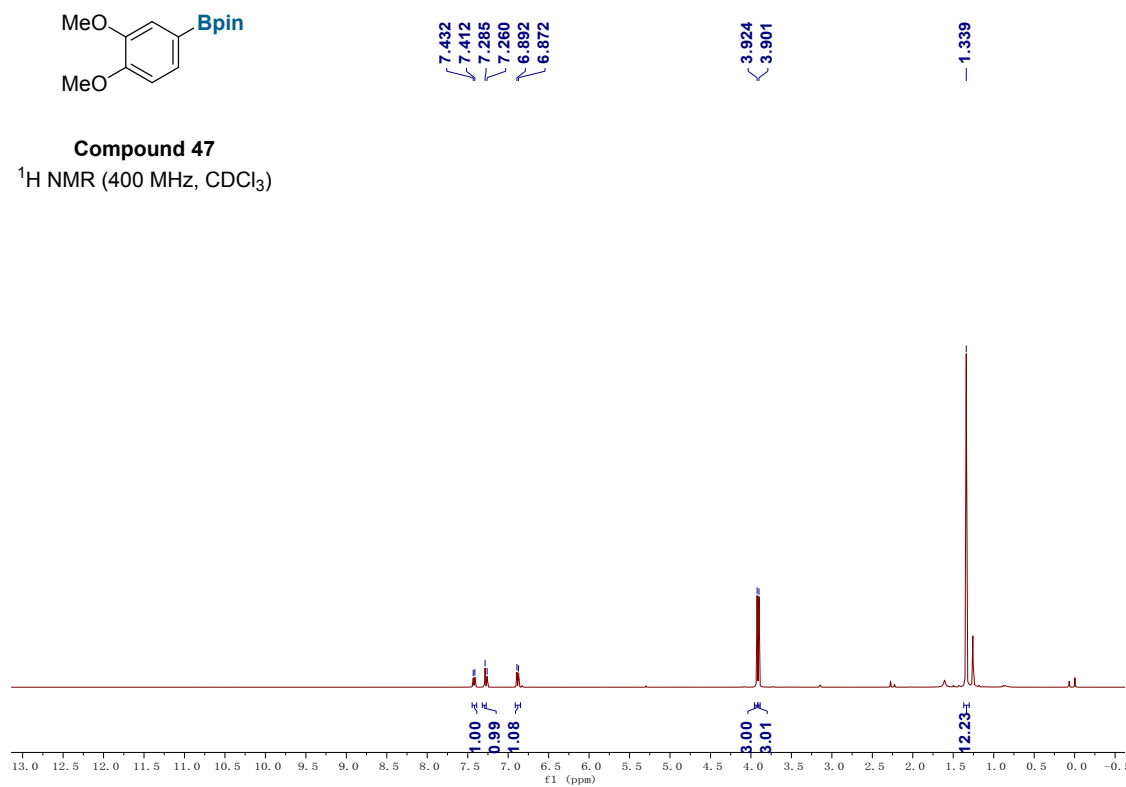**Compound 46**

^{13}C NMR (400 MHz, CDCl$_3$)

2-(3,4-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (47)

Compound 47
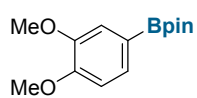
^{1}H NMR (400 MHz, CDCl$_3$)

Compound 47

^{13}C NMR (100 MHz, CDCl$_3$)

151.78
148.49
128.70
116.70
110.63
83.80
77.48
77.16
76.84
55.99
55.88
24.99
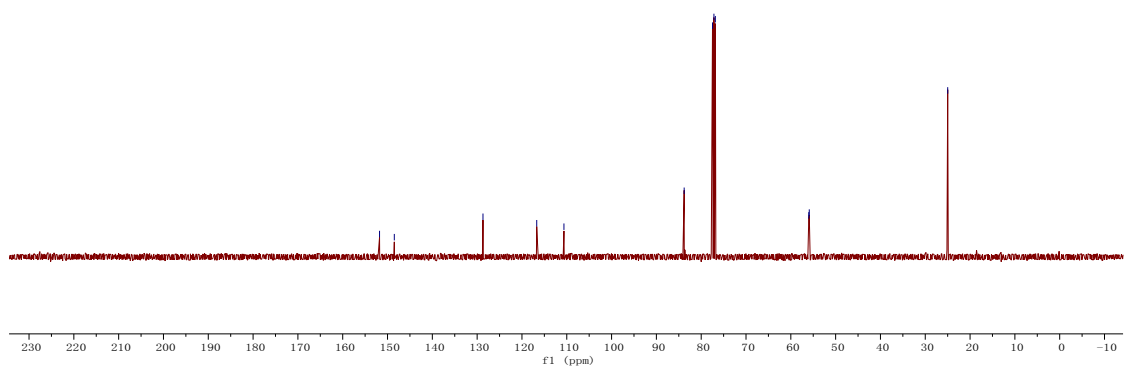
2-(4-(ethoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48)
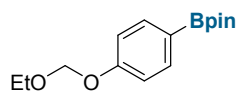
Compound 48

^{1}H NMR (400 MHz, CDCl$_3$)

7.761
7.740
7.260
7.039
7.018
5.253
3.746
3.728
3.711
3.693
1.331
1.228
1.210
1.193

2.00
2.02
2.12
2.11
12.20
3.13

13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
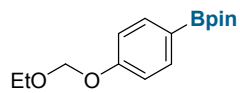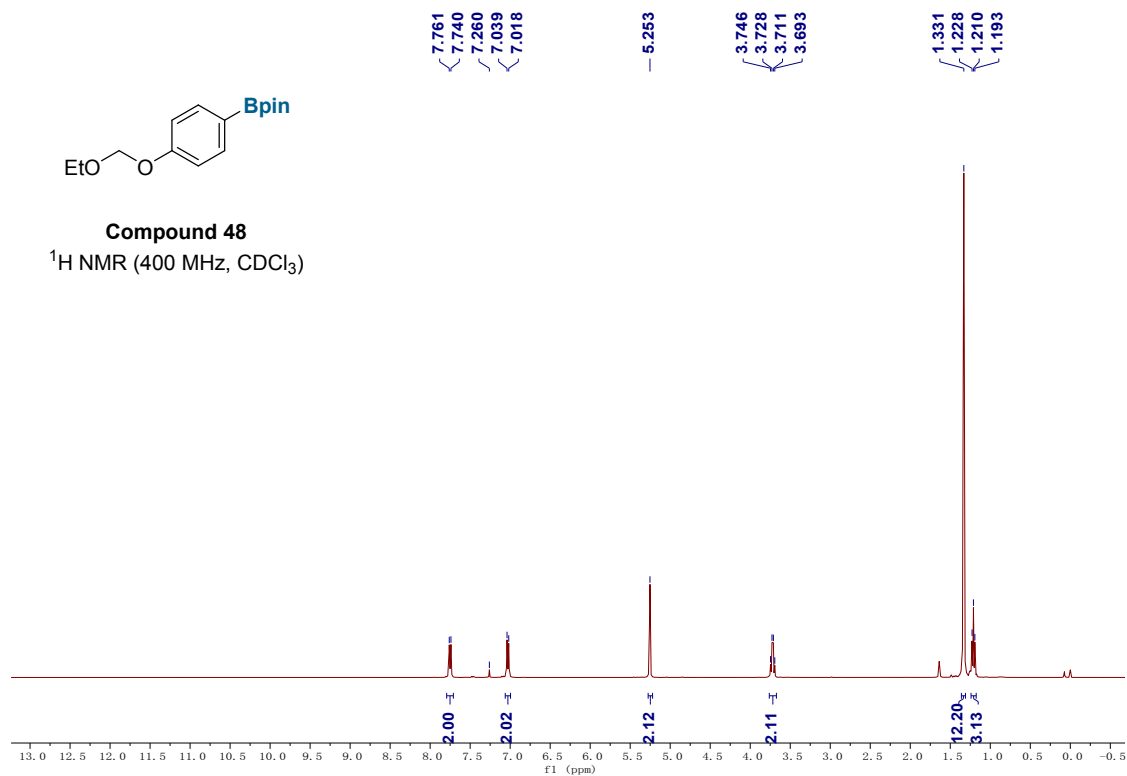
Compound 48

^{13}C NMR (100 MHz, CDCl$_3$)

160.06
136.59
115.53
92.88
83.71
77.48
77.16
76.84
64.43
24.98
15.23

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

88

2-(4-ethylpiperazin-1-yl)-4-(4-(triethylsilyl)phenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine (49).

Compound 49
^{1}H NMR (400 MHz, CDCl$_3$)

Compound 49

^{13}C NMR (100 MHz, CDCl$_3$)

159.88, 157.40, 151.58, 141.87, 136.26, 133.89, 127.85, 123.09, 106.11, 77.48, 77.16, 76.84, 52.89, 52.60, 45.68, 35.64, 31.76, 30.75, 26.73, 26.64, 25.97, 12.10, 7.61, 3.49

Compound 50

^{1}H NMR (400 MHz, CDCl$_3$)

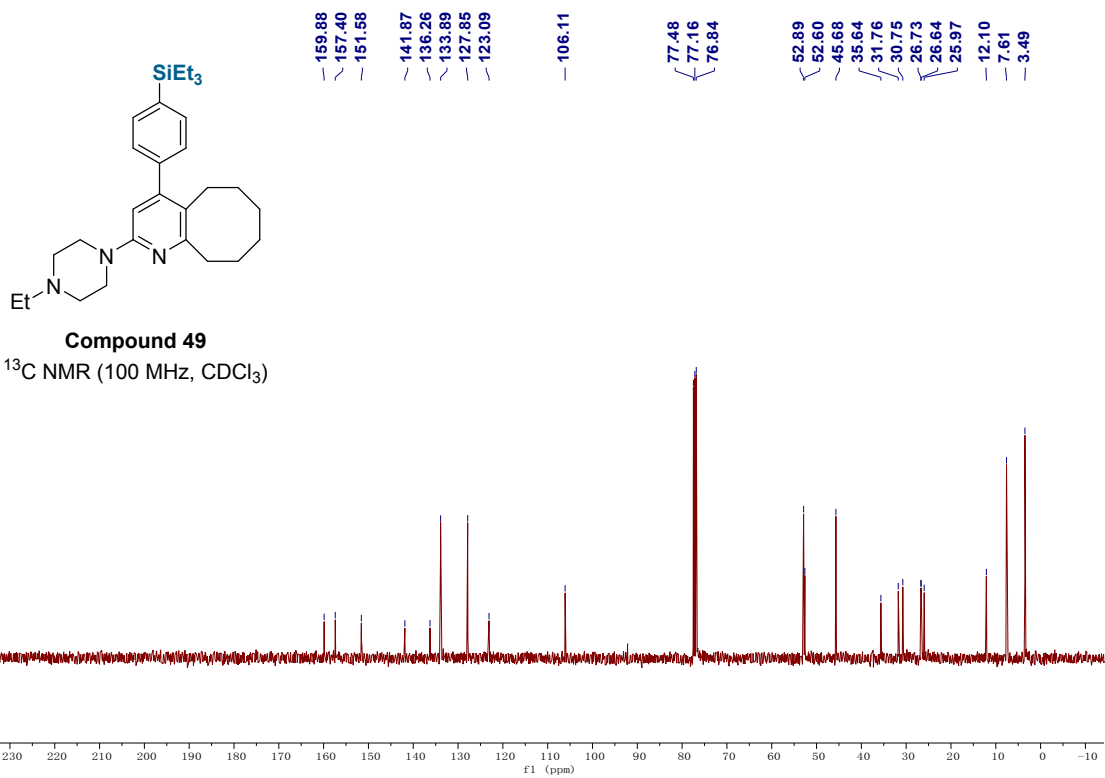7.409, 7.390, 7.260, 7.186, 7.168, 6.620, 6.599, 6.339, 6.130, 6.110, 5.869, 3.603, 3.595, 3.579, 3.572, 3.484, 3.464, 3.443, 3.276, 3.267, 3.243, 3.034, 3.006, 2.393, 0.967, 0.948, 0.929, 0.793, 0.774, 0.755, 0.735

90

154.51
148.21
144.28
141.57
135.55
134.67
127.01
107.92
105.65
101.17
98.10
77.48
77.16
76.84
69.76
59.65
56.31
46.51
44.28
41.71
34.04
7.58
3.49

Compound 50

^{13}C NMR (100 MHz, CDCl$_3$)

Triethyl(2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)silane (52).
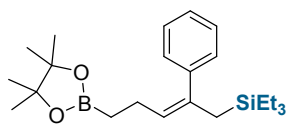
7.319
7.299
7.267
7.260
7.252
7.233
7.194
7.177
7.161
5.455
5.438
5.421
2.278
2.260
2.241
2.223
1.992
1.245
0.950
0.931
0.911
0.837
0.817
0.797
0.393
0.373
0.353
0.334

^{1}H NMR (400 MHz, CDCl$_3$)

1.91
2.16
1.12
1.02
2.03
2.00
12.00
2.19
8.95
6.09

^{1}C NMR (100 MHz, CDCl$_3$)

145.42
137.27
128.45
128.03
126.75
126.42
83.14
77.48
77.16
76.84
24.97
23.82
16.19
7.40
3.92